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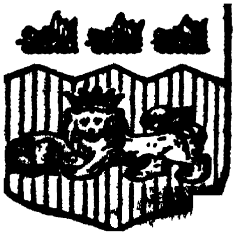

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KINEMATICAL THEORY AND GENERAL RELATIVITY

By

D. N. MOGHE

1. INTRODUCTION

THERE have been many attempts to explain Milne's Kinematical Theory on the basis of the general theory of Relativity. As the kinematical theory is due primarily to the application of the notions of the theory of sets of points and the fact that the particles in receding motion are supposed to form a statistical system, it is not perhaps logical to give an interpretation of the theory in terms of the ideas of general relativity. Even then, some of the interpretations given so far appear to bring out clearly a parallelism between general relativity and the kinematical theory. This parallelism is not, however, perfect as in such attempts $G(\xi)$ is replaced by $G(X)$. A more general case is represented by $G(X, \xi)$. We shall now examine these two cases in some detail.

2. CASE I—G (X)

It was Walker(¹) who first gave the line-element for this case, *viz.*,

$$ds^2 = \left\{ F(X) \right\}^2 \left[dt^2 - \frac{1}{c^2} \left(dr^2 + r^2 d\theta^2 + r^2 \sin^2 \theta d\phi^2 \right) \right] \ldots (1)$$

the notation being the same as usual. From the condition of isotropy we get the value of F (X) as

$$F(X) - (aX+b)^{1} \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

Gilbert(²) has considered a special case of this, namely, $b - 0$ and $a = t_0^2$ which gives $G(\xi) = -1$ ultimately. The geodesic equations (obtained either from the variational principle or by direct substitution in the differential equations for the geodesics) give for the tracks of particles the law of motion :

$$\ddot{r} = (r - \dot{r}t)\frac{Y}{X} \quad \frac{2X}{F}\frac{dF}{dX} + r\left(\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2\right) \quad \ldots\ldots \quad (3)$$

So that, when $\dot{\theta} = 0$, $\dot{\phi} = 0$, we get the familiar equations of Milne, *viz.*,

$$\ddot{r} = (r - \dot{r}t)\frac{Y}{X} G(X) \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

$$\text{where } G(X) = \frac{2X}{F}\frac{dF}{dX} = -\frac{2aX}{aX+b} \qquad \ldots\ldots\ldots\ldots\ldots\quad (5)$$

Another case for $a = -k^2$, $b = 1$ has been found convenient for the kinematical treatment.[8] It gives the line-element (1) the form

$$ds^2 = \frac{dt^2 - \frac{1}{c^2}\left(dr^2 + r^2\, d\theta^2 + r^2 \sin^2\theta d\phi^2\right)}{(1 - k^2 X)^2} \qquad \ldots\ldots\ldots\quad (6)$$

The notation in the reference cited being slightly different. With the aid of the transformation ics$=s$, ict$=x^\circ$, and the transformation from the spherical polars to the cartesian co-ordinates we have the conformal representation of (6) as

$$ds^2 = \frac{\sum\limits_{r=0}^{3} (dx^r)^2}{\left\{1 - k^2 \sum\limits_{r=0}^{3} (x^r)^2\right\}^2} \qquad \ldots\ldots\ldots\ldots\ldots\quad (7)$$

which shows that the manifold V4 is a hypersphere of constant curvature (radius R) and is embedded in an Euclidean flat space S5. We have, therefore

$$\frac{1}{R^2} = \frac{4k^2}{c^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\quad (8)$$

For the line-element (6), we get

$$8\,\pi\, T_1^1 = 8\,\pi\, T_2^2 = 8\,\pi\, T_3^3 = 8\,\pi\, T_4^4 = 12\,k^2 \qquad \ldots\ldots\quad (9)$$

$$\text{and} \qquad \rho\, oo = (\rho - 3p) = \frac{6k^2}{\pi} = \frac{3c^2}{2\,\pi\, R^2} \qquad \ldots\ldots\quad (10)$$

For the type of motion considered by Milne the relativistic analogue of the kinematical system should satisfy the condition of isotropy. In the present case it is satisfied. Milne's world model has also been shown to be an expanding universe of the hyperbolic type[4]. We now pass on to the more general case.

3. CASE II—G (X,ξ)

The line-element for this case is assumed to be of the form:

$$ds^2 = \left\{ F(X,\xi) \right\}^2 \left[dt^2 - \frac{1}{c^2}\left(dr^2 + r^2 d\theta^2 + r^2 \sin^2\theta d\phi^2\right) \right] \ldots (11)$$

Calculating the components of the Riemann—Christoffel tensor for this case and writing the condition of isotropy as

$$B'_{ijmn} = k\;(g_{im}g_{nj} - g_{ij}g_{nm}) \qquad \ldots\ \ldots\ldots\ldots\quad (12)$$

Where k is the Riemannian curvature, we have the following set of differential equations for the determination of F (X, ξ), *viz.*,

$$\frac{\partial^2 F}{\partial r^2} - \frac{1}{r}\frac{\partial F}{\partial r} - \frac{2}{F}\left(\frac{\partial F}{\partial r}\right)^2 = \frac{1}{r^2}\left\{\frac{\partial^2 F}{\partial \theta^2} - \frac{2}{F}\left(\frac{\partial F}{\partial \theta}\right)^2\right\},$$

$$(\text{also} \because T^{1}_{1} = T^{2}_{2} = T^{3}_{3}) \qquad \ldots\ldots\;\ldots \qquad (13)$$

$$\frac{\partial^2 F}{\partial r d\theta} - \frac{\partial F}{\partial \theta}\left(\frac{1}{r} + \frac{2}{F}\frac{\partial F}{\partial r}\right) = o, \ (\text{also} \because T^{2}_{1} = o = T^{1}_{2}) \ldots\ldots \qquad (14)$$

$$\frac{\partial^2 F}{\partial r dt} - \frac{2}{F}\frac{\partial F}{\partial r}\cdot\frac{\partial F}{\partial t} = o, \ (\text{also} \because T^{4}_{1} = o = T^{1}_{4}) \qquad \ldots\ldots \qquad (15)$$

and

$$\frac{\partial^2 F}{\partial \theta \partial t} - \frac{2}{F}\cdot\frac{\partial F}{\partial \theta}\cdot\frac{\partial F}{\partial t}\cdot = o, \ (\text{also} \because T^{4}_{2} = o = T^{2}_{4}) \ldots\ldots \qquad (16)$$

From these differential equations it is desirable to get a solution in the form F $\equiv$F (X, ξ). Such a solution does not seem to be possible. This negative result should compare favourably with G (ξ) being perfectly arbitrary. The (r, t) geodesics give the track equations:

$$\ddot{r} = (r - \dot{r}t)\,\frac{Y}{X}\cdot\frac{2\,(XF_1 - \xi F_2)}{F}$$

$$+ r\,(\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2)\left(1 - \frac{2\xi F_2}{F}\right) \qquad \ldots\ldots \qquad (17)$$

Where $F_1 = \frac{\partial F}{\partial X}$, $F_2 = \frac{\partial F}{\partial \xi}$. Putting $\dot{\theta} = o$, $\dot{\phi} = o$, we get

$$\ddot{r} = (r - \dot{r}t)\,\frac{Y}{X}\,G\,(X, \xi) \qquad \ldots\ldots\ldots\ldots\ldots \qquad (18)$$

Where $$G\,(X,\xi) = \frac{2\,(XF_1 - \xi\,F_2)}{F} \qquad \ldots\ldots\ldots\ldots\ldots \qquad (19)$$

If we assume $$F\,(X, \xi) = X^m\,\phi\,(\xi) \qquad \ldots\ldots\ldots\ldots\ldots \qquad (20)$$

We obtain $$G\,(\xi) = 2\left(m - \frac{\xi\phi'}{\phi}\right) \qquad \ldots\ldots\ldots\ldots\ldots \qquad (21)$$

Where a dash denotes a differentiation w. r. t. ξ. As ϕ and ϕ' are quite arbitrary functions of ξ so is G (ξ). The energy tensor has the following surviving components, *viz.*,

$$8\pi T^{1}_{1} = \frac{c^2}{F^3}\frac{\partial F}{\partial r}\left(\frac{4}{r} + \frac{3}{F}\frac{\partial F}{\partial r}\right) + \frac{c^2}{r^2 F^3}\left\{2\frac{\partial^2 F}{\partial \theta^2} + 2\cot\theta\,\frac{\partial F}{\partial \theta}\right.$$

$$\left. - \frac{1}{F}\left(\frac{\partial F}{\partial \theta}\right)^2\right\} - \frac{1}{F^3}\left\{2\frac{\partial^2 F}{\partial t^2} - \frac{1}{F}\left(\frac{\partial F}{\partial t}\right)^2\right\} \quad \ldots\ldots \qquad (22)$$

$$8\pi T_2^2 = 8\pi T_3^3 = \frac{c^2}{F^3}\left\{2\frac{\partial^2 F}{\partial r^2} + \frac{2}{r}\frac{\partial F}{\partial r} - \frac{1}{F}\left(\frac{\partial F}{\partial r}\right)^2\right\} + \frac{c^2}{r^2F^3}\frac{\partial F}{\partial \theta}$$

$$\left(2\cot\theta + \frac{3}{F}\frac{\partial F}{\partial \theta}\right) - \frac{1}{F^3}\left\{2\frac{\partial^2 F}{\partial t^2} - \frac{1}{F}\left(\frac{\partial F}{\partial t}\right)^2\right\} \quad \ldots\ldots\ldots \quad (23)$$

$$8\pi T_4^4 = \frac{c^2}{F^3}\left\{2\frac{\partial^2 F}{\partial r^2} + \frac{4}{r}\frac{\partial F}{\partial r} - \frac{1}{F}\left(\frac{\partial F}{\partial r}\right)^2\right\} + \frac{c^2}{r^2F^3}\left\{2\frac{\partial^2 F}{\partial \theta^2}\right.$$

$$\left. + 2\cot\theta - \frac{1}{F}\left(\frac{\partial F}{\partial \theta}\right)^2\right\} - \frac{3}{F^4}\left(\frac{\partial F}{\partial t}\right)^3 \quad \ldots\ldots\ldots\ldots \quad (24)$$

Hence, we conclude that although the kinematical theory accepts special relativity in principle an exact analogue from the general theory of relativity is not possible.

Note

It is found that if we consider the line-element,

viz., $$ds^2 = \{F(X,\xi)\}^2\left[dt^2 - \frac{1}{c^2}(dx^2 + dy^2 + dz^2)\right] \ldots \quad (i)$$

we get the geodesics in the form

$$x = (x - \dot{x}t)\frac{Y}{X} \cdot - \frac{2(XF_1 - \xi F_2)}{F} \quad \ldots\ldots\ldots\ldots \quad (ii)$$

where we may write

$$G(X,\xi) = \frac{2(XF_1 - \xi F_2)}{F} \quad \ldots\ldots\ldots\ldots \quad (iii)$$

If, however, we propose to have

$$G(\xi) = \frac{2(XF_1 - \xi F_2)}{F}, \quad \ldots\ldots\ldots \quad (iv)$$

F must be supposed to be of the form $X^m f(\xi)$. Keeping

G (ξ) arbitrary we get

$$F = X^n \xi^m e^{-\int \frac{G(\xi)}{2(\xi)} d\xi} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (v)$$

Here, the energy-tensor is given by the components

$$-8\pi T_1^1 = -\frac{c^2}{F^2}\left[3\left\{\frac{1}{F}\frac{\partial^2 F}{\partial x^2} - \frac{1}{F^2}\left(\frac{\partial F}{\partial x}\right)^2\right\} + \left\{\frac{1}{F}\frac{\partial^2 F}{\partial y^2}\right.\right.$$

$$\left. + \frac{1}{F^2}\left(\frac{\partial F}{\partial y}\right)^2\right\} + \left\{\frac{1}{F}\frac{\partial^2 F}{\partial z^2} + \frac{1}{F^2}\left(\frac{\partial F}{\partial z}\right)^2\right\} - \frac{1}{c^2}\left\{\frac{1}{F}\frac{\partial^2 F}{\partial t^2}\right.$$

$$\left.\left. + \frac{1}{F^2}\left(\frac{\partial F}{\partial t}\right)^2\right\}\right] + \frac{3c^2}{F_3}\left(\frac{\partial^2 F}{\partial x^2} + \frac{\partial^2 F}{\partial y^2} + \frac{e^2 F}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2 F}{\partial t^2}\right) \ldots. \quad (vi)$$

and similar expressions for T_2^2 and T_3^3 ; and

$$\begin{aligned}-8\pi T_4^4 = -\frac{c^2}{F^2}\Bigg[&\left\{\frac{1}{F}\frac{\partial^2 F}{\partial x^2}+\frac{1}{F^2}\left(\frac{\partial F}{\partial x}\right)^2\right\}\\ &+\left\{\frac{1}{F}\frac{\partial^2 F}{\partial y^2}+\frac{1}{F^2}\left(\frac{\partial F}{\partial y}\right)^2\right\}\\ &+\left\{\frac{1}{F}\frac{\partial^2 F}{\partial z^2}+\frac{1}{F^2}\left(\frac{\partial F}{\partial z}\right)^2\right\}-\frac{3}{c^2}\left\{\frac{1}{F}\frac{\partial^2 F}{\partial t^2}-\frac{1}{F^2}\left(\frac{\partial F}{\partial t}\right)\right\}\Bigg]\\ &+\frac{3c^2}{F^3}\left(\frac{\partial^2 F}{\partial x^2}+\frac{\partial^2 F}{\partial y^2}+\frac{\partial^2 F}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2 F}{\partial t^2}\right) \qquad \ldots\ldots\ldots \text{(vii)}\end{aligned}$$

For a perfect fluid, therefore, we have $T = \rho - 3p = o$, or $\Box F = o$ ... (viii)

where

$$\Box = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}-\frac{1}{c^2}\frac{\partial}{\partial t^2}.$$

(viii) is the well-known equation of wave propagation.

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(2) C. Gilbert: Quart. J Maths, 9, 35, 185-193, (1938).
(3) G. C. McVittie: Cosmological Theory (Methuen & Co., 1937), p. 74
(4) *Ibid.*, p. 95.

A NOTE ON ISOTROPIC MANIFOLDS

By

D. N. MOGHE

1. INTRODUCTION

THE purpose of this short paper is to bring out clearly some properties of isotropic manifolds which have an application to the theory of relativity.

In a previous paper(1) I have examined the condition of isotropy of relativity manifolds from the point of view of differential geometry. There, it was found convenient to use the geodesic form of line-element for a space Vn, *viz.*,

$$ds = dt^2 + g_{ij} dx^i dx^j \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where the formula for the Riemannian curvature was found to be

$$K = \tfrac{1}{4} g^{im} g^{jl} \frac{\partial g_{il}}{\partial t} \cdot \frac{\partial g_{jm}}{\partial t} - \tfrac{1}{2} g^{im} \frac{\partial^2 g_{im}}{\partial t^2} \qquad \ldots\ldots\ldots\ldots \quad (2)$$

We propose to show in the next section that the condition of isotropy makes the principal components of the energy tensor equal to each other.

2. ENERGY TENSOR

The energy tensor is usually expressed as :

$$-8\pi T^{\nu}_{\mu} = G^{\nu}_{\mu} - \tfrac{1}{2} g^{\nu}_{\mu} (G - 2\lambda) \qquad \ldots\ldots \quad (3)$$

where $Gij = Kg_{ij} = \lambda g_{ij}$ (2), so that $G = (n-1) K$. Therefore, (3) can be simplified to the form :

$$-8\pi T^{\nu}_{\mu} = K\delta^{\nu}_{\mu} - \tfrac{1}{2} (\overline{n-1}\, K - 2.\, \overline{n-1}\,.K)\delta^{\nu}_{\mu}$$

$$= \frac{n+1}{2} K\delta^{\nu}_{\mu} \qquad \ldots\ldots\ldots\ldots \quad (4)$$

which clearly shows that all the cross-components of T^{ν}_{μ} vanish because $\delta^{\nu}_{\mu} = o$ for $\mu \mp \nu$. In particular,

$$-8\pi T^{1}_{1} = \frac{n+1}{2} K \quad \text{, etc.,} \qquad \ldots\ldots\ldots \quad (5)$$

where K is given by (2). There will be a slight change in the R.H.S of (4) and (5) in the relativistic case where the g_{ij}'s are written with a negative sign. No further elucidation on this point is necessary as particular cases have already been given by several writers.

3. GEODESICS

Differential equations for the geodesics can be written in the form

$$\frac{d^2x^i}{dt^2} + \{jl, i\} \frac{dx^j}{dt}\frac{dx^l}{dt} - \{jl, o\} \frac{dx^j}{dt}\frac{dx^l}{dt}\frac{dx^i}{dt} = o , \quad .. \quad (6)$$

which for the line-element (1) further simplifies to :

$$\frac{d^2x^i}{dt^2} + \{jl, i\} \frac{dx^j}{dt}\frac{dx^l}{dt} + \frac{1}{2}\frac{\partial g_{jl}}{\partial t}\frac{dx^j}{dt}\frac{dx^l}{dt}\frac{dx^i}{dt} = o , \quad \ldots\ldots \quad (7)$$

Also, line-element (1) is expressed as :

$$\left(\frac{ds}{dt}\right)^2 = 1 + g_{ij}\frac{dx^i}{dt}\frac{dx^j}{dt} \qquad \ldots\ldots\ldots\ldots \quad (8)$$

which after differentiation w.r.t.t. and slight reduction yields

$$g_{ij}\frac{d^2x^i}{dt^2}\frac{dx^j}{dt} + \frac{\partial g_{ij}}{\partial t}\frac{dx^i}{dt}\frac{dx^j}{dt} = o \qquad \ldots\ldots\ldots \quad (9)$$

Hence, with the help of (9), (7) can be modified as :

$$\frac{d^2x^i}{dt^2} - \frac{1}{2} g_{jl}\frac{d^2x^j}{dt^2}\frac{dx^l}{dt}\frac{dx^i}{dt} + \{jl, i\}\frac{dx^j}{dt}\frac{dx^l}{dt} = o \quad .. \quad (10)$$

Similarly, we have

$$\frac{d^2x^j}{dt_2} - \frac{1}{2} g_{il}\frac{d^2x^i}{dt^2}\frac{dx^l}{dt}\frac{dx^j}{dt} + \{il, j\}\frac{dx^i}{dt}\frac{dx^l}{dt} = o. \quad .. \quad (11)$$

Multiplying (10) by g_{m} $\frac{dx^m}{dt}$ and (11) by g_{jk} $\frac{dx^k}{dt}$ and subtracting the latter result from the former, we get

$$\left(g_{im}\frac{d^2x^i}{dt^2}\frac{dx^m}{dt} - g_{jk}\frac{d^2x^j}{dt^2}\frac{dx^k}{dt}\right) -$$

$$\frac{1}{2}\left(g_{jl}\, g_{im}\frac{d^2x^j}{dt^2}\frac{dx^i}{dt}\frac{dx^m}{dt} - g_{il}\, g_{jk}\frac{d^2x^i}{dt^2}\frac{dx^j}{dt}\frac{dx^k}{dt}\right)\frac{dx^l}{dt}$$

$$+ \left\{ [jl, m]\frac{dx^j}{dt}\frac{dx^m}{dt} - [il, k]\frac{dr^i}{dt}\frac{dx^k}{dt}\right\}\frac{dx^l}{dt} = o \quad .. \quad (12)$$

The middle term on the L. H. S. of (12) vanishes on slight reduction and interchange of dummy suffixes. Consequently, we obtain

$$\left\{ g_{im} \frac{d^2x^i}{dt^2} + [jl, m] \frac{dx^j}{dt} \frac{dx^l}{dt} \right\} \frac{dx^m}{dt}$$

$$= \left\{ g_{jk} \frac{d^2x^j}{dt^2} + [il, k] \frac{dx^i}{dt} \frac{dx^l}{dt} \right\} \frac{dx^k}{dt} \qquad (13)$$

Writing $p_m = g_{im} \dfrac{d^2x^i}{dt^2} + [jl, m] \dfrac{dx^j}{dt} \dfrac{dx^l}{dt}$, we can express

(13) in the condensed form :

$$p_m \dot{x}^m = p_k \dot{x}^k \qquad \ldots\ldots\ldots \quad (14)$$

where $\dot{x}^m = \dfrac{dx^m}{dt}$. (14) shows that $p_m \dot{x}^m$ is invariant.

4. GEODESIC CURVATURE

$$\text{Let } P^i = \frac{d^2x^i}{ds^2} + \left\{ jl, i \right\} \frac{dx^j}{ds} \frac{dx^l}{ds} \qquad \ldots\ldots\ldots\ldots \quad (15)$$

define the geodesic curvature vector. The covariant component is given by

$$P_k = g_{ik} \frac{d^2x^i}{ds^2} + g_{ik} \left\{ jl, i \right\} \frac{dx^j}{ds} \frac{dx^l}{ds} \qquad \ldots\ldots \quad (16)$$

Then, the condition that this defines the geodesic curvature is that

$$P_k x'^k = 0 \, , \quad \frac{dx^k}{ds} = x'^k \qquad \ldots\ldots \quad (17)$$

(17) can be expressed as

$$- \frac{dg_{ik}}{ds} \frac{dx^i}{ds} \frac{dx^k}{ds} + [jl, k] \frac{dx^j}{ds} \frac{dx^l}{ds} \frac{dx^k}{ds} = 0 \quad \ldots \quad (18)$$

Remembering that $[jl, k] + [kl, j] = \dfrac{\partial g_{jk}}{\partial x^l}$, we reduce (18) to the simple form, *viz.*,

$$2 \frac{\partial g_{ik}}{\partial t} \cdot \frac{dx^i}{dt} \frac{dx^k}{dt} + [jk, i] \frac{dx^j}{dt} \frac{dx^k}{dt} \frac{dx^i}{dt} = 0 \quad \ldots\ldots \quad (19)$$

From (19), (13) and (9) we get

$$p_k \dot{x}^k = 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (20)$$

REFERENCES

(1) "On Isotropic Manifolds in the Theory of Relativity," Proc. Ind. Acad. Sci., X 4, pp. 275-278, 1939.

(2) *loc. cit.*, Equation (11), p. 276.

It will not be out of place to note here that there is a slip in equation (14) of the paper cited above. On the R. H. S. of (14), $k/(n-1)$ should be written instead of k. Similarly, a corresponding numerical correction is required in the subsequent equations. There is, however, no damage to the results obtained as we can write $K' = k/(n-1)$.

ON INTEGRAL FUNCTIONS OF INFINITE ORDER

By

S. M. SHAH, M.A. (LOND.)

LET $f(z)$ be an integral function. In a previous note* I considered how large $\log M(r)/n(r)$ can be for functions of finite order. I state here a similar result for functions of infinite order.

Theorem *Given* $\psi(x)$ *any positive non decreasing function such that*

$$(1) \qquad \lim_{x \to \infty} \frac{\log \psi(x)}{\log x} = \infty$$

there exists an Integral function $F(z)$ *of infinite order for which*

$$(2) \qquad \limsup_{r \to \infty} \frac{T(r, F)}{\psi(r)\, n(r, F)} = \infty$$

$$(3) \qquad \limsup_{r \to \infty} \frac{T(r, F)}{\psi(r)\, N(r, 1/F)} = \infty$$

and an integral function $f(z)$ *of infinite order for which*

$$(4) \qquad \liminf_{r \to \infty} \frac{\psi(r)\, T(r,f)}{n(r,f)} = 0$$

Proof:

Let— $\lambda_n = n^{n^n}$; $\mu_n = \lambda_n^{[\psi(\lambda_n)]+1}$; $B_o = 2$

$$B_n = Max \left\{ [\psi^3(\lambda_n)]+1,\ B^3_{n-1} \right\},\ A_n = [\log B_n/n]+1$$

$$f(z) = \prod_{1}^{\infty} \left\{ 1 + \left(\frac{z}{\lambda_n}^{\mu_n} \right) \right\},\ F(z) = \prod_{1}^{\infty} \left\{ 1 + \left(\frac{z}{\lambda_n} \right)^{A_n} \right\}^{B}$$

$f(z)$ and $F(z)$ are integral functions, of infinite order and satisfy (4) and (2), (3) respectively.

MUSLIM UNIVERSITY,
ALIGARH.

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*Bulletin American Math. Soc., 46 (1940) 909-912. $M(r)$, $n(r, F-a)$, $N(r, 1/F-a)$ and $T(r)$ have the usual meanings. *cf.* E. C. Titchmarsh, Theory of Functions, 1939, Ch. 8.

ON THE RELATIONS BETWEEN THE LOWER ORDER AND THE EXPONENT OF CONVERGENCE OF ZEROS OF AN INTEGRAL FUNCTION

By

S. M. SHAH, M.A. (LOND.)

1. LET P and λ denote the order and the lower order of integral function $f(z)$ and let P_1 and λ_1 denote the exponent of convergence and the lower order of zeros of $f(z)$. In the usual notation we have

$$\begin{array}{c}P\\ \lambda\end{array} = \frac{\lim}{r\to\infty}\ \frac{\log\log M(r)}{\log r};\quad \begin{array}{c}P_1\\ \lambda_1\end{array} = \frac{\overline{\lim}}{r\to\infty}\ \frac{\log n(r)}{\log r}$$

I have proved a relation elsewhere between these four numbers for[1] the functions of order less than one. In this note I give a number of examples suitably constructed so as to bring out all the possible relations between these four numbers.

2. If $P = 0$ then we have $P = P_1 = \lambda = \lambda_1$

3. If P be positive and non-integer then $P = P_1$ If $P = \lambda$ then $P_1 = \lambda_1$ and conversely, we may have $P = \lambda = \lambda_1$ ($\cos \sqrt{z}$) or $P > \lambda = \lambda_1$ (Ex. 1) or $P > \lambda > \lambda_1$ (Ex. 2). We note however that given P and λ_1 such that $0 < P < 1, 0 \leqslant \lambda_1 \leqslant P$, λ cannot be arbitrarily chosen since[2]

$$\lambda_1 \leqslant \lambda \leqslant \lambda_1 / (\lambda_1 + 1 - P)$$

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[1] S. M. Shah, The Lower Order of the Zeros of Integral Functions, in publication in Indian Math. Soc. J.

[2] A similar relation $\lambda \leqslant \psi(\lambda_1, P)$ may exist when $P \vee 1$ is noninteger, but I have not been able to prove it so far. It is seen from Ex. 2 that $\psi(\lambda_1, P)$ must be not less $[P]$.

Ex. 1. Given P $(o < P < \infty)$ there exists an integral function $f(z)$ of order P for which $P = P_1 > \lambda = \lambda_1$

Let $C_n = n^{n^n}$, $k = 1 + [P]$, $\mu_n = \left[C_n^P\right]$; $f(z, P) =$

$$\prod_1^\infty \left\{ 1 + \left(\frac{z}{c_n}\right)^{k\mu_n} \right\}$$

Then $f(z, P)$ is a C. P. of order P and[3] genus $[P]$ for which $\lambda = \lambda_1 = o$

Ex. 2. Given $P \geqslant 1$ there exists a C. P. of order P for which $\lambda_1 = o$; $\lambda > o$

Let $F(z) = (1 - z) \exp\left\{ z + \ldots\ldots + \frac{z^p}{p} \right\} f(z, P)$

where $p = [P]$ and $f(z, P)$ is defined in Ex. 1. $F(z)$ is a C. P. of order P and genus p. We have $\lambda_1 = o$. Further

$$M(r) \geqslant |F(r)| \geqslant 1 - r \quad \exp\left(r + \ldots + \frac{r^p}{p} \right)$$

Hence $\lambda \geqslant p > o$. It is easily seen that $\lambda = p$. If we take now P as an integer we have —

Ex. 3. Given positive integer P, there exists a C. P. of order P for which $P = P_1 = \lambda > \lambda_1$

Ex. 4. Given P $o, < P < \infty$ there exists a C. P. of order P for which $o < \lambda_1 < \lambda < P_1 = P$

Let $A_n = 2^{2^{n-1}}$ $(n \geqslant 1)$, $a_o = o$, $k = 1 + [P]$, $\xi_n = \left[a_n^{P/k}\right] -$

$$\left[a_{n-1}^{P/k}\right]; \quad \mathrm{H}(z) = \prod_1^\infty \left\{ 1 + \frac{z^k}{a_n} \right\}^{\xi_n}$$

H (z) is a C. P. of order P and genus $[P]$ for which[1]

$$\lambda_1 = P/2 \, ; \; \lambda = P / \{ 2 - (P/k) \}$$

4. If P is an integer there are five alternatives.[4]

(*a*) $P_1 < P$ then $P = \lambda$ We may have $P > P_1 = \lambda_1$ (Ex. 5) and $P > P_1 > \lambda_1$ (Ex. 6).

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[3] *cf.* S. M. Shah, Bulletin American Math. Soc., 46, 909—912 ; c. p. means canonical product.

[4] G. Valiron, Lectures on the General Theory of Integral Functions, p. 59.

Ex. 5. $f(z) = \exp(z^P) \operatorname{Cos} \sqrt{z}$

Ex. 6. Let $0 < P_1 < P$ and $G(z) = \exp(z^P) f(z, P_1)$ where f is defined in Ex. 1 ; $G(z)$ is of order P for which $0 = \lambda_1 < P_1 < \lambda = P$

(*b*) $P = q = p = P_1$. We have

(*i*) $P = \lambda_1$ for $\frac{1}{\Gamma(z)} = z e^{\gamma z} \prod \left\{ \left(1 + \frac{z}{n}\right) \exp\left(-\frac{z}{n}\right) \right\}$

(*ii*) $\lambda_1 < \lambda < P$ for

$$J(z) = \exp\left(-\frac{z^P}{P}\right) \left\{ (1 - z) \exp\left(z + \dots + \frac{z^P}{P}\right) H(z) \right\}$$

Where H (z) is defined in Ex. 4. $J(z)$ is of order P for which $\lambda_1 = P/2$ and $\lambda = \frac{P}{\{2 - P/(1+P)\}}$

(*iii*) $\lambda_1 = \lambda < P$ for $I(z) = \exp\left(-z - \frac{z^2}{2} \dots - \frac{z^P}{P}\right) \left\{ (1 - z) \exp\left(z + \dots \dots \frac{z^P}{P}\right) f(z, P) \right\}$ where f (z, P) is defined in Ex. 1. We have $\lambda_1 = \lambda = 0$

(*iv*) $\lambda_1 < \lambda = P$ for F $(z) = \exp(z^P)$ f (z, P) where f (z, P) is defined in Ex. 1. We have $\lambda_1 = 0$ and $\lambda = P$.

(*c*) $P_1 = P = p$; $q < P$ We have

(*i*) $P = \lambda = \lambda_1$ for $\frac{\operatorname{Sin} z}{z}$ (*ii*) $P = \lambda > \lambda_1$ (Ex. 3).

(*iii*) $P > \lambda = \lambda_1$ (Ex 1) (*iv*) $P > \lambda > \lambda_1$ (Ex. 4).

Ex. 7. $K(z) = \prod^{\infty} \left\{ 1 + \frac{z}{n(\log n)^2} \right\}$

Here $P = \lambda_1 = 1$; $p = 0$

Ex. 8. $S(z) = \prod_{1}^{\infty} \left\{ 1 + \frac{z^P}{n^2 a_n} \right\}^{a_n}$; $a_n = 2^{2^{n-1}}$

Here $\lambda_1 = P/2$; $\lambda = P_1 = P$; $p = P - 1$; $q = 0$

Ex. 9. $U(z) = \prod_{1}^{\infty} \left\{ 1 + \left(\frac{z}{c_n}\right)^{P\theta_n} \right\}$; $c_n = n^n$; $\theta_n = \left[\frac{P}{C_n} \Big/ n^2 \right]$

Here $\lambda_1 = \lambda = 0 = q$; $p = P - 1$

(*d*) $P_1 = P = q$; $p = P - 1$ We shall prove that $P = \lambda$

Lemma *If $f(z)$ be of integral order P and such that lim inf log $M(r)/r^P = 0$ and $\sum 1/r_n^P$ be convergent then $f(z)$ is of genus $P - 1$.*

We suppose $f(0) = 1$ and hence $f(z) = P(z)$ *exp* $\{ Q(z) \}$ where $P(z)$ is c.p. of genus $\leqslant P - 1$ and $Q(z)$ a polynomial of degree $q \leqslant P$. Let

$R_1 < R_2 < \dots$ be an indefinitely increasing sequence such that log $M(R_n) < \in R_n^P$ and let $k > 1$. The annulus $\frac{R_n}{k} \leqslant |z| \leqslant R_n$ contains atleast one circle on which(5) $\log |P(z)| > -H \log M_1(kr)$ where $M_1(r) = \underset{z=r}{Max} |P(z)|$.

Now

$Log\, M_1(kr) < \in k^P r^P$ if $r > r_0$ *i. e.*, if $n > n_0(\in)$ since $R_n / k \leqslant r \leqslant R_n$.

Hence for $n > n_1 > n_0$

$\log |f(z)| \leqslant \log M(r) < \log M(R_n) < \in R_n^P < \in k^P r^P$

$$\frac{R\{Q(z)\}}{r^P} = \frac{\log |f(z)|}{r^P} - \frac{\log |P(z)|}{r^P} < \in k^P + H \in k^P$$

Hence

$$\liminf_{r \to \infty} \frac{Max\, R\{Q(z)\}}{r^P} = 0$$

And so $Q(z)$ is a polynomial of degree $q \leqslant P-1$ which proves the lemma. Since by hypothesis (d), $P = q$ we must have $\liminf \log M(r)/r^P > 0$ from which we get $P = \lambda$.

(i) $P = \lambda_1$ *for* $f(z) = exp(z)\, K(z)$

(ii) $P > \lambda_1$ *for* $f(z) = exp(z^P)\, S(z)$

Where K and S are defined in Ex. 7 and 8.

(e) $P_1 = P;\ p = P - 1,\ q < P$

(i) $P = \lambda = \lambda_1$ (*Ex.* 7); (ii) $P > \lambda = \lambda_1$ (*Ex.* 9);

(iii) $P = \lambda > \lambda_1$ (*Ex.* 8); (iv) $P > \lambda > \lambda_1$.

If $P \geqslant 2$ we consider

$$f(z) = (1 - z)\, exp \left\{ z + \dots \frac{z^{P-1}}{P-1} \right\} U(z)$$

where $U(z)$ is defined in Ex. 9. $f(z)$ is c. p. of order P, genus $P-1$ for which $\lambda_1 = 0$; $\lambda = P - 1$

If $P=1$ then let $a_1 = 2$; $b_m = [2\sqrt{a_n}]$; $a_{m+1} = b_m^3$.

$$f(z) = \prod_{m=1}^{\infty} \left\{ \prod_{\sqrt{a_m} \leqslant n \log^2 n < a_m} \left(1 + \frac{z}{n \log^2 n}\right) \prod_{a_m \leqslant n^2 \leqslant b^m} 1 + \frac{z}{n^2} \prod_{b_m < n \log^2 n < \sqrt{a_{m+1}}} \left(1 + \frac{z}{n \log^2 n}\right) \right\}$$

$f(z)$ is c. p. of order 1, genus zero for which $\lambda_1 = 1/2$; $\lambda = 2/3$.

Muslim University,
Aligarh

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[5] Valiron, *loc. cit.*, p. 89.

A CASE OF THE PRODUCT OF CERTAIN DEMLO-NUMBERS

By

PROFESSOR M. L. CHANDRATREYA, M.A.,

AND

D. R. KAPREKAR, B.SC., S.T.C.

(1) IN the article on 'Product with Super-wonderful Demlo-Numbers' B. U. Journal, March 1942, the product of any such number as $W^9_n = 12345678\ (9)_n\ 87654321$ with any given number has been put down as the result of subtracting Q from the central part of the number $QT\ (9)_{n-1}T$. We shall show that the product of some demlo-numbers reduces to these products of super-wonderful demlo-numbers.

(2) For this purpose we shall define one or two terms. Any demlo-number is of the type $M\ (r)_n\ P$ where $M+P = (r)_n$. If P contains K digits then M also contains the same theoretically, and then the quantity $n+k$ is called the *length of the demlo-number.* Thus the length of the demlo-number 134888888754 is $6+3=9$.

It is shown in the article 'General Expression for the Product of Demlo-Numbers,' B. U. Journal November 1940, that any demlo-number $M\,(r)_n P$ can be expressed as $D \times (1)_l$ where $D=(9M+r)$ and l is the length of that demlo-number. This quantity $(9M+r)$ may be called as the *demlofying number* or *demlofier.* Thus the number given above has $D=(9 \times 134+8)=1214$, and therefore can be written as $1214 \times (1)_9$.

(3) It is easily seen that the product of two demlo-numbers can therefore be written down as $D \times D' \times (1)_l \times (1)_{l'}$ where l, l' are the lengths of these two numbers and D, D′ are their demlofiers. The product $(1)_l \times (1)_{l'}$ has been discussed completely in the B. U. Journal, November 1941, and it is shown there that when any one of *l and l′* is equal to nine, and the other equal to or greater than nine, the product is W^9_p where $p=l'+1-9$ supposing $l' > l$ or equal to l which is nine. Thus the product of two such demlo-numbers can be written down as the product of a number with a super-wonderful demlo-number.

(4) An illustration may be given. Thus to find
$81(8)_7\,07 \times 1782\,(4)_9\,2662$

Here the lengths are 9 and 13 and the demlofiers are $9 \times 81 + 8 = 737$ and $9 \times 1782 + 4 = 16042$. Thus the product is

$$737 \times 16042 \times (1)_9 \times (1)_{13}$$

The product $(1)_9 \times (1)_{13} = W^9_5$ for $p = 13 + 1 - 9$

Hence the required product reduces to

$$737 \times 16042 \times W^9_5 = 11822954 \times W^9_5$$

Here $Q = 145962$, $R = 32$ $L = 395061728$

$L' = 604938271$, $T = 394915765 = L - (Q+1)$

$T' = L' + (Q+1) = 605084234$

Hence, finally subtracting Q from the central part of $QT\,(9)_{n-1}T'$ we get the product

$$145962394915751403760 5084234$$

College of Fngineering, Poona
Khare's Wada, Deolali

AN INEQUALITY IN PARTITIONS

By

HANSRAJ GUPTA, M.A., PH.D.

1. DENOTING by $p_k(n)$ the number of partitions of n into exactly k summands, or what is the same thing, into summands the greatest of which is k; the writer has shown[1] in an elementary manner that

For values of $k \geqslant 1$,

$$\binom{n-1}{k-1} \leqslant k!\, p_k(n) \leqslant \binom{n+\frac{k(k-1)}{2}}{k-1}. \qquad (1)$$

In the paper referred to above, this result is made to follow from the identity

$$p_k(n) - p_k(n-k) = p_{k-1}(n-1). \qquad (2)$$

In this note, I prove that

For values of $k \geqslant 4$, and $n \geqslant n_k$ where n_k depends upon k alone.

$$\binom{n+k-1+a_k-1}{k-1} \leqslant k!\, p_k(n+k) \leqslant \binom{n+k-1+a_k}{k-1}. \qquad (3)$$

with $a_k = \dfrac{k(k-1)}{4}$.

In fact, if ε be any pre-assigned positive quantity however small, following my argument, it could be proved that

For values of $n \geqslant n_{\varepsilon,k}$ $k \geqslant 4$,

$$\binom{n+k-1+a_k-\varepsilon}{k-1} \leqslant k!\, p_k(n+k) \leqslant \binom{n+k-1+a_k}{k-1}. \qquad (4)$$

Hence for large values of n, we have the asymptotic formula :

$$k!\, p_k(n) \backsim \binom{n-1+a_k}{k-1}, \quad \text{where } a_k = \frac{k(k-1)}{4}. \qquad (5)$$

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[1] In the Proc. Indian Acad. Sci., 16, 1942, pp. 101-2.

In what follows, we write $x^{(k)}$ for $x\ (x-1)\ (x-2)\ (x-3) \ldots (x-k+1)$; and G (m, r) denotes the sum of the products of the first m natural numbers taken r at a time.

2. My proof of (3) is indicated in the following lines.

Let $\binom{n+k-2+b_{k-1}}{k-2} \leqslant (k-1)!\, p_{k-1}(n+k-1) \leqslant \binom{n+k-2+a_{k-1}}{k-2}$

$k \geqslant 5$;

except for a finite number of values of n ; a_{k-1} and b_{k-1} being certain functions of k alone. Then since

$$\begin{aligned} p_k\ (n+k) &= p_{k-1}\ (n+k-1)\ +\ p_k\ (n) \\ &= p_{k-1}\ (n+k-1)\ +\ p_{k-1}\ (n-1)\ +\ p_{k-1}\ (n-k-1) + \ldots \\ &\qquad + p_{k-1}\,(n-rk-1), \end{aligned}$$

where $r = [n/k]-1$; to show that

$$\binom{n+k-1+b_k}{k-1} \leqslant k\,!\,p_k(n+k) \leqslant \binom{n+k-1+a_k}{k-1}$$

except for a finite number of values of n, all that we need find are suitable values of a_k and b_k, such that for every $n \geqslant$ some positive integer m_k,

$$\binom{n+k-1+a_k}{k-1} - \binom{n-1+a_k}{k-1} > K\binom{n+k-2+a_{k-1}}{k-2}, \quad (6)$$

and $$\binom{n+k-1+b_k}{k-1} - \binom{n-1+b_k}{k-1} < K\binom{n+k-2+b_{k-1}}{k-2}. \quad (7)$$

Now, we notice that

$$\begin{aligned} &(x+k-1)^{(k-1)} - (x-1)^{(k-1)} \\ &= (x+1)\,(x+2)\,(x+3) \ldots (x+k-1) - (x-1)\,(x-2)\,(x-3) \ldots (x-k+1) \\ &= 2 \sum_{r=1}^{[k/2]} G\,(k-1,\ 2r-1)\ x^{k-2r}, \\ &= k\ (k-1)\ \left\{ x^{k-2} + \binom{k}{4} x^{k-4} + \tfrac{1}{8}\binom{k}{6}(3k^2-7k-2)\, x^{k-6} + \ldots \right\}. \quad (8) \end{aligned}$$

The right side of (8) is $> k\ (k-1) \left(x+\frac{k-3}{2} \right)^{(k-2)}$, $k \geqslant 4$.

Moreover, it is $< k\ (k-1)\left(x^2 + \frac{k^{(3)}}{12} \right)^{\frac{k-2}{2}}$, $k \geqslant 4$;

which is $< k\ (k-1)\ (x+\frac{k-3}{2}+\varepsilon)^{(k-2)}$; $\quad (9)$

provided $2\,\varepsilon\,x - \left(\frac{k-3}{2}\right)^2 \geqslant \frac{k^{(3)}}{12}$,

i.e., if $x \geqslant \frac{k^3}{24\varepsilon}$, In particular if $\varepsilon = \frac{1}{2}$, the condition that (9) may hold is that

$$x \geqslant \frac{k^3}{12}. \tag{10}$$

Thus (6) holds if $a_k + \frac{k-3}{2} = k-2+a_{k-1}$,

i.e., if $a_k - a_{k-1} = \frac{k-1}{2}$.

Hence $a_k = \frac{k\,(k-1)}{4}$.

And (7) holds if $b_k + \frac{k-2}{2} = k-2+b_{k-1}$;

so that $b_k = \frac{(k-1)\,(k-2)}{4} = a_{k-1}$.

From (10) it appears that (3) holds if $n_k = O(k^3)$.

Since $p_1\,(n) = 1$, $p_2\,(n) = \lfloor n/2]$, and $p_3\,(n) = [(n^2+3)/12]$;
(5) holds for all values of $k \geqslant 1$.

GOVERNMENT COLLEGE,
HOSHIARPUR

LECTURE NOTES

By

B. B. BAGI

(1) Van der Monde's Theorem

THIS theorem is proved in books on Algebra by the help of a certain theorem in the theory of Algebraic Equations. This note contains an elementary proof by induction.

In the usual notation, the theorem may be stated thus :

For all values of m and n,

$$(m+n)_r = m_r + C_1^r\, m_{r-1}\, n_1 + C_2^r\, m_{r-2}\, n_2 + \dots\dots$$

Assuming the truth of the theorem for the integer r, we shall prove that it holds for the next integer namely $r+1$.

Thus $(m+n)_{r+1}$

$$= (m+n)_r\,(m+n-r)$$

$$= [m_r + C_1^r\, m_{r-1}\, n_1 + C_2^r\, m_{r-2}\, n_2 + \dots]\,(m+n-r).$$

Now $m_r\,(m+n-r) = m_r\,(m-r) + m_r\, n$

$$= m_{r+1} + m_r\, n_1\ .$$

$$m_{r-1}\, n_1 (m+n-r) = m_{r-1}\, n_1\,(m-r+1) + m_{r-1}\, n_1\,(n-1)$$

$$= m_r\, n_1 + m_{r-1}\, n_2.$$

Similarly $m_{r-2}\, n_2\,(m+n-r) = m_{r-1}\, n_2 + m_{r-2}\, n_3,$

etc. etc.

$$\therefore (m+n)_{r+1} = m_{r+1} + m_r\, n_1 + C_1^r\,(m_r\, n_1 + m_{r-1}\, n_2)$$

$$+ C_2^r\,(m_{r-1}\, n_2 + m_{r-2}\, n_3) + \dots$$

$$= m_{r+1} + (C_0^r + C_1^r)\, m_r\, n_1$$

$$+ (C_1^r + C_2^r)\, m_{r-1}\, n_2 + \dots$$

$$= m_{r+1} + C_1^{r+1}\, m_r\, n_1 + C_2^{r+1} m_{r-1}\, n_2 + \dots$$

Now $(m+n)_1 = m+n = m_1+n_1$

Hence the theorem holds when $r=1$.

Therefore it holds when $r=2$, etc.

We observe that if in the Binomial Theorem

$$(m+n)_r = m_n + C^r_1 \; m^{r-1} \; n^1 + C'_2 \; m^{r-2} \; n_2 \; + \ldots\ldots$$

we change the indices of m, n into suffixes we get Van der Monde's Theorem.

Applying the same process to the Multinomial Theorem

$$(m_1 + m_2 + m_3 + \ldots)^n = \Sigma \; m_1^p \; m_2^q \ldots \; \frac{n\,!}{p\,!\;q\,!\ldots}$$

where p, q, r, ... are positive integers such that $p+q+r+\ldots = n$, we get an extension of Van der Monde's Theorem, namely,

$$(m_1 + m_2 + m_3 + \ldots)_n = \Sigma \; (m_1)_p (m_2)_q \ldots \; \frac{n\,!}{p\,!\;q\,!\ldots}$$

where p, q, ... are chosen as above.

(2) Equation to Cone with Given Conic for Base

TO find the equation to the cone whose vertex is the point (α, β, γ) and base the conic

$$f(x, y) \equiv ax^2 + 2hxy + by^2 + 2gx + 2fy + c = o, \; z = o \qquad (1)$$

This problem is solved in §63 of Bell's Solid Geometry, by a long and complicated method. A neater and shorter one is given below :

Let (x, y, z) be any point on the cone and let the line joining (α, β, γ) to (x, y, z) meet the above conic in a point dividing the joint of these points in the ratio $\lambda : 1$.

Thus $\left(\dfrac{\alpha+\lambda x}{1+\lambda}, \dfrac{\beta+\lambda y}{1+\lambda}, \dfrac{\gamma+\lambda z}{1+\lambda}\right)$ lies on the conic (1).

$$\therefore \quad f\left\{\frac{\alpha+\lambda x}{1+\lambda}, \frac{\beta+\lambda y}{1+\lambda}\right\} = o \qquad (2)$$

and $\quad \gamma + \lambda z = o \qquad (3)$

When γ is eliminated between (2) and (3), we get the required equation in the form

$$f\left(\frac{\alpha z - \gamma x}{z-\gamma}, \frac{\beta z - \gamma y}{z-\gamma}\right) = o \qquad (4)$$

The form given in the book may be reached as follows :

If $F(x, y, t) \equiv ax^2 + 2hxy + by^2 + 2gxt + 2fyt + ct^2$

then $F(\alpha + \lambda x, \beta' + \lambda y, \gamma' + \lambda t)$

$$= F(\alpha', \beta', \gamma') + \lambda \left\{ x \frac{\partial F}{\partial \alpha'} + y \frac{\partial F}{\partial \beta'} + t \frac{\partial F}{\partial \gamma'} \right\}$$

$$+ \lambda^2 F(x, y, t).$$

On writing $\alpha' = \alpha$, $\beta' = \beta$, $\gamma' = t = 1$ in this we get

$$F(\alpha + \lambda x, \beta + \lambda y, 1 + \lambda)$$

$$= f(\alpha, \beta) + \lambda \left\{ x \frac{\partial f}{\partial \alpha} + y \frac{\partial f}{\partial \beta} + \left(\frac{\partial F}{\partial \gamma} \right)_{\gamma=1} \right\}$$

$$+ \lambda^2 f(x, y)$$

Now (2) is equivalent to

$$F(\alpha + \lambda x, \beta + \lambda y, 1 + \lambda) = o$$

i.e.,

$$f(\alpha, \beta) + \lambda \left\{ x \frac{\partial f}{\partial \alpha} + y \frac{\partial f}{\partial \beta} + \left(\frac{\partial F}{\partial \gamma} \right)_{\gamma=1} \right\}$$

$$+ \lambda^2 f(x, y) = o \qquad (5)$$

Eliminating λ between (3) and (5) we get the form given in the book.

KARNATAK COLLEGE,
DHARWAR

INTERPOLATION AND SUMMATION FORMULAS AND THE PROPERTIES OF FACTORIALS—I

By

DR. D. K. SEN

§ 1. INTRODUCTORY

1. In an article "A Note on Interpolation Formulas," published in the Journal of the University of Bombay, Vol. IV, Part II, 1935, I advocated the use of only two interpolation formulas of Newton's, one for equal and the other for unequal intervals of the argument. Attention was also drawn to the fact that best results can be expected when interpolation is carried out near the middle of the *effective* interval, the term "effective" implying the interval defined by the data actually included in the formula used for calculation. Many previous writers have discussed the comparative merits of the various interpolation formulas. Burn and Brown write in *Elements of Finite Differences* :

"Central differences. therefore, do not appear to possess any considerable value, since with the same data we can quite as easily obtain the same results with ordinary differences."

"If any of the adjustments in central differences are employed there is always the risk of obtaining a worse instead of a better result, as is necessarily the case in any arbitrary adjustment."

Fraser in his Notes published in J. I. A., Vol. 50, pp. 17-18, writes · "Any formula which goes outside the track of the central differences introduces coefficients which are larger than the corresponding coefficients of a central difference formula, and the farther the formula departs from central differences the more does the relative magnitude of the coefficients increase."

Again on p. 21 of his Notes, Fraser admits the necessity of a study of the properties of the coefficients, for "it is simply in the properties of the binomial coefficients that the explanation of the value of the central differences is to be found."

The conclusions of the two preceding paragraphs were arrived at by Fraser from the consideration of a number of particular cases. There were no other rigorously valid grounds for his assertions, or for those of Steffensen and Sasuly given below.

Steffensen (*Interpolation*, p. 41) writes, "... interpolation with descending or ascending differences is necessary at the beginning and end of a table, *as central differences are not to be had there*" (italics mine).

Milne-Thomson (*Calculus of Finite Differences*, p. 58) and Sasuly (*Trend Analysis of Statistics*, p. 30) express the same opinion as Steffensen.

Whittaker and Robinson (*Calculus of Observations*, p. 49) have attempted to demonstrate the superiority of a central difference formula over Newton's formula with ordinary differences, by showing that the error in interpolating *near the mid-range* with the former is less than that in interpolating *near the beginning* with the latter. But they have overlooked the fact that for a true comparison of the two formulas interpolation *in the same region* was necessary. Further, they have mentioned, without assigning any reason for the same, on p. 60, that it is best to use Stirling's formula when $-\frac{1}{4}<x<\frac{1}{4}$, and Bessel's formula when $\frac{1}{4}<x<\frac{3}{4}$.

Sheppard (Proc. London Math. Soc., 1906, *4*) writes :

"The formulæ considered are the values of u_θ corresponding to $x_\theta = x_0 + \theta h$, where θ in the ordinary formula lies between 0 and 1, and in the central difference formula lies either between 0 and 1 or between $-\frac{1}{2}$ and $+\frac{1}{2}$."

There is no reason advanced as to the necessity of imposing these limits.

Sheppard, however, admits on p. 334 of this paper that "the advancing difference formula which we use for interpolating through the interval x_p to x_{p+1}, Θ having values from 0 to 1, would become the central difference formula if we used it for interpolating through the interval from $x_{p+n-\frac{1}{2}}$ to $x_{p+n+\frac{1}{2}}$, Θ having values from $n-\frac{1}{2}$ to $n+\frac{1}{2}$ when differences are taken upto those of $(2n)$-th order, or through the interval from x_{p+n} to x_{p+n+1}, Θ having values from n to $n+1$ when differences are taken upto those of $(2n+1)$-th order."

In view of the above remarks one wonders why Sheppard did not advocate interpolation, as far as possible, near the mid-range, whichever formula was being used. His insistence on different ranges of interpolation for the two types of formulas is again to be met with on p. 337 where he says, "Suppose that through the range of x from x_0 to x_m, $f^{m+1}(x)$ is approximately constant or at any rate does not vary greatly. Then the magnitude of the residual error depends on the magnitude of $\theta(\theta-1)(\theta-2)....(\theta-m)$. This is *obviously* (italics mine) less when θ is nearly equal to $\frac{1}{2}m$ than when it is nearly equal to 0; if for instance, $m=5$ and we are interpolating at the middle of an interval the above expression when we use the advancing difference formula, is

$$-\tfrac{1}{2}\cdot\tfrac{1}{2}\cdot\tfrac{3}{2}\cdot\tfrac{5}{2}\cdot\tfrac{7}{2}\cdot\tfrac{9}{2};$$

but when we use the central difference formula, it is

$$-\tfrac{5}{2}\cdot\tfrac{3}{2}\cdot\tfrac{1}{2}\cdot\tfrac{1}{2}\cdot\tfrac{3}{2}\cdot\tfrac{5}{2},$$

which is ess than one-fourth of the former. Thus, by the use of central differences we may be able to exclude a term which would otherwise have to be included, and thus shorten our formulæ."

As I have pointed out before, a true comparison of formulas must be based on results corresponding to the same region of the given interval and not on those which are derived in different regions as has obviously been done by Sheppard.

In a second paper (Proc. London Math. Soc., 1911, *10*, 149) Sheppard has further shown, by consideration of what he terms as the *tabular triangle*, that the error of a formula can be diminished "by replacing the formula by a more central one ; in other words, the central difference formula gives a smaller limit of tabular error than any formula of this kind, involving the same number of consecutive values of *u*."

If I wish to paraphrase the above statement, it means that the more central the region of interpolation, the less is the error.

These have led me to undertake a detailed study of the properties of the factorial-functions (or simply factorials as they are generally called) which play an important role in the theory of interpolation—and summation—formulas. I have then studied the latter formulas in the light of knowledge thus gained and have been able to come to definite conclusions. I have used the notations of Steffensen throughout the present paper.

The discussion on the interpolation formulas would, however, be incomplete without a few remarks about Aitken's new process of iterated interpolation (Proc. Edin. Math. Soc., 1932, *3*, 56-76), although the present paper deals exclusively with formulas involving equal intervals of the argument. Aitken's method consists of repeated linear interpolation with divided differences, firstly for pairs of values corresponding to $x=a,\ b\ ;\ a,\ c\ ;\ a,\ d\ ;....$; then to triplets of values corresponding to $x=a,\ b,\ c\ ;\ a,\ b,\ d\ ;\ ....$; and so on. It can be seen that a value thus obtained at any stage corresponding to a set of given values of *x*, is merely the Newton's interpolation polynomial involving divided differences which would be obtained by the given set of values of the argument and those of the function. As Milne-Thomson has remarked (*loc. cit.*, p. 77), "The process is therefore completely equivalent to interpolation with Newton's general divided difference formula. . . . If then interpolation by Newton's formula be practicable, the numbers in later columns will tend to equality as the work proceeds. This leads to a simplification, since in the linear interpolation these figures at the beginning which are common to all the members of a column can be dropped. The process terminates when further interpolation would cease to influence the result."

This method of iterated interpolation is particularly convenient when an arithmometer is used for calculation. The advent of this method, which is by the way the same as Newton's formula for unequal intervals (and which includes the formula for equal intervals as a special case), has taken away as it were, the prop of the so-called superiority of the central difference formulas.

Mention might be made in this connection of a similar iterative process developed by Neville (Jubilee Commemoration Volume of Ind. Math. Soc., pp. 87-120). Unlike Aitken's process where the calculations start from one end of the interval, Neville's method has been developed in order of the nearness of the given values to the value to be interpolated.

2. The basic formula is the identity

$$\begin{aligned} f(x) = {} & f(a_0) + (x-a_0)\,f(a_0, a_1) \\ & + (x-a_0)\,(x-a_1)\,f(a_0, a_1, a_2) + \;\ldots\ldots \\ & + (x-a_0)\,(x-a_1)\ldots\ldots\;(x-a_{n-1})\,f(a_0, a_1, a_2, \ldots\ldots a\;) \\ & + \;R, \end{aligned}$$

where the remainder-term

$$R = (x-a_0)(x-a_1)\ldots\ldots(x-a_{n-1})(x-a_n)\,f(x, a_0, a_1, \ldots\ldots a_n).$$

Steffensen has shown (*loc. cit.*, pp. 23-24) that

$$f(x, a_0, a_1, \ldots\ldots a_n) = \frac{f^{n+1}(\xi)}{n+1\,!},$$

where f^{n+1} denotes the $(n+1)$-th derivative of $f(x)$, and ξ is some number lying between the greatest and the least of x, a_0, a_1, $\ldots\ldots a_n$. In practical application of interpolation the remainder-term is usually omitted, and therefore the degree of accuracy of any interpolation formula will be judged by the magnitude of the corresponding remainder-term. The remainder-terms in the various interpolation formulas are as follow :

(*i*) Newton's formula after $(n+1)$ terms,

$$R = \frac{x^{(n+1)}}{(n+1)\,!}\,f^{n+1}\,(\xi),$$

where ξ lies between the greatest and least of x, o and n.

(*ii*) Stirling's formula after $(2n+1)$ terms,

$$\mathrm{R} = \frac{x^{[2n+2]-1}}{(2n+1)\,!}\,f^{2n+1}\,(\xi),$$

where ξ lies between the greatest and least of x, n and n.

(*iii*) Bessel's formula after $2n$ terms,

$$\mathrm{R} = \frac{x^{[2n+1]-1}}{(2n)\,!}\,f^{2n}\,(\xi),$$

where ξ lies between the greatest and least of x, $-n+\frac{1}{2}$ and n $\frac{1}{2}$.

(*iv*) Everett's first formula after $2n$ terms,

$$\mathrm{R} = \frac{(x-n)\,x^{[2n]-1}}{(2n)\,!}\,f^{2n}\,(\xi),$$

and Everett's second formula after $(2n+1)$ terms,

$$\mathrm{R} = \frac{(x-n-\frac{1}{2})\,x^{[2n+1]-1}}{(2n+1)\,!}\,f^{2n+1}\,(\xi),$$

with similar ranges of existence for ξ.

(*v*) Gauss's formulas, of which (*ii*), (*iii*) and (*iv*) are special cases, have the following forms for R:

$$\frac{x^{[2n+2]-1}}{(2n+1)!}f^{2n+1}(\xi),\ \frac{(x\pm n)x^{[2n]-1}}{(2n)!}f^{2n}(\xi),$$

$$\frac{x^{[2n+1]-1}}{(2n)!}f^{2n}(\xi),\ \frac{[x\pm(n+\frac{1}{2})]x^{[2n+1]-1}}{(2n+1)!}f^{2n+1}(\xi).$$

3. Regarding the range of values of x, it appears (*Cf.* the statements quoted in Art. 1) that the previous workers have taken it for granted that the value of x to be used should not exceed unity, but no reason has been put forward as to why this should be the case. If, however, we examine any interpolation formula, central or otherwise, it will be found that x occurs in the factorials involved in each term of the formula and in the remainder-term. The other coefficients involve differences of $f(x)$ for given values of x, *viz.*, $0, \pm 1, \pm 2, \ldots$, or, $\pm\frac{1}{2}, \pm\frac{3}{2}, \ldots$ and are thus independent of the values of x, chosen for the purpose of interpolation; they depend, however, on the length of the interval. Once the origin and the unit (for the scale) of x has ben settled, and the values of the differences are known from the table, one is at liberty to utilise the interpolation formula for any value of x that one likes, provided that it is situated in the range of the given table, or slightly beyond it for the purpose of extrapolation. The distinction between the formulas with central differences and those with advancing differences is that in the former the origin is situated near the centre of the table whereas in the latter it is situated at one end.

As I have remarked elsewhere and as we shall see later on, the best results are to be obtained for values of x near the centre, although this value may exceed unity, whichever interpolation formula be used.

4. *Effect of change of origin and the size of the interval on the accuracy of the result obtained from interpolation formulas with equal intervals, the number of intervals remaining the same.*

It has been remarked by Steffensen and justly so (*loc. cit.*, p. 34), that it is not possible to interpolate for every function and for every range. Only the consideration of the magnitude of the remainder-term should be the criterion of applicability of an interpolation formula to a given problem.

Every term of a formula except R, consists of two main factors, (1) a factorial, and (2) a difference; R is also made of two principal factors, *viz.*, a factorial and a derivative. When a table of a function and its differences are given, any *change of origin* of x would not alter the given values of the function and any difference. Thus the second factor of every term is unaltered by this change of origin. The value of each first factor, however,—even of R,—undergoes the change with x. The change of origin is in fact the same as a change in the value at which interpolation is to be performed without affecting the values of the other quantities in the formula.

Next, we shall consider the effect of the change of the measure of the interval of the argument. Let the new interval be h times the old one, that is, the new argument x' is h times that of the old argument x. Since the measures of the corresponding values of the arguments are the same, namely x, in terms of their respective units, the first factor, *viz.*, the factorial, retains the same value. The second factor, however, takes up different values. The remainder-terms which measure the comparative degree of accuracy in the two cases, have only the second factor, *viz.*, the derivative, affected by the change in the length of the intervals. For instance let

$$R=A\left[\frac{d^n}{dx^n}f(x)\right]_{x=\xi},$$

in the first case, where A denotes the unaffected factor. And in the second case we shall have the value of the first derivative as

$$\underset{x_2\longrightarrow x_1}{\mathrm{Lt}}\ \frac{f(x_2h)-f(x_1h)}{x_2-x_1}=\left[\frac{d}{dx}f(xh)\right]_{x=x_1}$$

Therefore, the remainder-term o.

$$R'=A\left[\frac{d^n}{dx^n}f(xh)\right]_{x=\xi}=h^n A\left[\frac{d^n}{dx'^n}f(x')\right]_{x'=\xi'}.$$

If the value of the n-th derivative does not change much within the range under consideration, the remainder-term is changed to about h^n times the previous value. Thus we can considerably enhance the degree of accuracy of the interpolation formula by choosing h sufficiently small. On the other hand, if h be large enough, the error in the interpolated result would be great enough to make interpolation useless.

Example.—Find an upper limit to the length of an interval so that the error after taking three terms of Newton's formula would be less than $.0001$, for $f(x)=\frac{1}{1+x^2}$, the number of intervals being four.

Let the length of each interval be h; so that the four intervals are defined by the end-values 0, h, $2h$, $3h$.

Here $$R=\frac{x^{(3)}}{3!}h^3f'''(\xi).$$

It will be found that the maximum value of $x^{(3)}$ in the interval (0, 2) or, even in a slightly greater interval, is $\frac{2\sqrt{3}}{9}$.

Further, $f'''(x)=\frac{24x(1-x^2)}{(1+x^2)^4}<24\,x<72h.$

Therefore, $R<\frac{8}{\sqrt{3}}h^4$.

The given condition will clearly be satisfied if $\frac{8}{\sqrt{3}}h^4<.0001$, or, $h<.068$ nearly.

It is easy to see that the above value will do for interpolation involving larger number of intervals than 4.

A table of maximum values of $x^{(n)}$, like the one given in this paper later on, will be useful for solving problems of this nature.

§ 2. PROPERTIES OF FACTORIAL-FUNCTIONS

5. *We shall use the notation* $F_n\ (x)$ for the product

$$x\,(x-1)\,(x-2)\ldots\ldots\,(x-n).$$

This is a polynomial of degree $(n+1)$, vanishing at the $(n+1)$ points, $x=0,\ 1,\ 2,\ \ldots,\ n$, and changing sign at each of these points. It retains the same sign in any interval $(r,\ r+1)$ where r is zero or a positive integer not greater than $(n-1)$. We are here mainly concerned in the behaviour of this function from $x=0$ to $x=n$. Its graph is, in the above region, of a wavy form cutting the x-axis at the points, $0.\ 1,\ 2,\ \ldots,\ n$. Thus the function has a maximum ordinate, irrespective of sign, in each of the sub-intervals $(r,\ r+1)$.

It is at once evident that when n is odd

$$F_n\ (n-x)=F_n\ (x),$$

and so the function is symmetrical *about the ordinate at the middle point* $x=\frac{1}{2}n$.

And, when n is even

$$F_n\ (n-x)=-F_n\ (x),$$

showing that the function is symmetrical *about the middle point* $x=\frac{1}{2}n$.

6. From the expression for the derivative, $F'_n\ (x)$, we get

$$F'_n\,(n-r)\ =(-1)^r\,.\,F'_n\,(r),$$

and $|\,F'_n\,(0)\,|>|\,F'_n\,(1)\,|>|\,F'_n\,(2)\,|\ldots>|\,F'_n\,(r)\,|$

so long as $r \ngtr \frac{1}{2}n$. The graph of $F_n\,(x)$ thus cuts the x-axis at smaller and smaller angles as we proceed from each end towards the centre of the complete interval $(0,\ n)$. Since the length of each of the sub-intervals $(r,\ r+1)$ is the same, the above indicates that the graph of $F_n\,(x)$ will have less and less deviation from the x-axis as we proceed from one interval to the next towards the central sub-interval.

7. Further, $F_n\,(x+1)$ and $F_n\,(x)$ have opposite signs when x lies in $(0,\ n)$, The ratio

$$\frac{F_n\,(x+1)}{F_n\,(x)}=-\frac{x+1}{n-x}$$

is less in magnitude than unity so long as $x+1<n-x$, or as $x<\frac{1}{2}(n-1)$. This demonstrates that $|\,F_n\,(x+1)\,|<|\,F_n\,(x)\,|$ as one proceeds to the middle of the interval $(0,\ n)$. Again

$$F_n\,(x)+F_n\,(x+1)\equiv 2x(x-1)\ldots.\,(x-n+1)\ \left(x-\tfrac{n-1}{2}\right)$$

is really the difference in magnitudes of the two quantities $F_n\,(x)$ and $F_n\,(x+1)$. A study of the signs of the right-hand side and those of $F_n\,(x)$

and $F_n(x+1)$, for different values of n and x, will again lead to the result that $|F_n(x+1)| < |F_n(x)|$, if $x<\frac{1}{2}(n-1)$.

Taking this result in conjunction with that of the previous article, one can assert that the magnitude of the maximum ordinate of $y=F_n(x)$ decreases from one sub-interval $(r, r+1)$ to another sub-interval nearer (or coincident with) the central one (or ones).

8. *Determination of the locations and the values of the greatest and the least of the maximum ordinates of* $F_n(x)$ *in the range* (o, n).

(*i*) When n is odd $(=2m+1)$, it is evident that the least of the maximum ordinates will occur at the centre, $x=\frac{1}{2}n$, of the given range, and that its value is

$$F_{2m+1}(m+\tfrac{1}{2}),\ \text{or},\ (-1)^{m+1}.\left\{\tfrac{1}{2}.\tfrac{3}{2}\ldots\frac{2m+1}{2}\right\}^2.$$

(*ii*) It is in general impossible to evaluate the exact values of x corresponding to the other maximum ordinates since they are the roots of an equation of degree n, *viz.*,

$$F'_n(x)=o. \qquad (1)$$

Turning first to the greatest, we know that it lies in the first-interval (0, 1). We therefore subdivide this into ten equal parts and try to determine in which of the smaller intervals the required root lies. We have

$$\frac{1}{F_n}\frac{dF_n}{dx}=\frac{1}{x}-\left(\frac{1}{1-x}+\frac{1}{2-x}\cdots\cdot+\frac{1}{n-x}\right). \qquad (2)$$

In the interval (0, 1), $F_n(x)$ has the same sign and hence the root of the equation $F'_n(x)=o$ can be located by finding when the sign of the right-hand side of (2) changes.

When $x=0.5$, the right-hand side is clearly negative. And, when x is very small, n remaining finite, the first term is large enough to make the right-hand side positive. The required root thus lies in (0, 0.5).

When $n=1$, this root is at $x=0.5$, and the greatest value of $F_1(x)$ is 0.25.

We shall now determine upto what value of n (>1), the root will lie in the interval (0.4, 0.5). We have, therefore, to find upto what value of n the right-hand side of (2) remains positive when $x=0.4$; that is, how far $10[\frac{1}{4}-(\frac{1}{6}+\frac{1}{16}+\frac{1}{26}+\cdots\cdot$ to n terms$)]$

will be positive. It is clear that n must be 2. In fact this root is $1-\sqrt{\frac{1}{3}}$ and the value of the maximum ordinate is $\frac{2}{9}\sqrt{3}$.

Similar procedure assisted by actual summation (which is not laborious in these cases) shows that the root of (1) lies in the interval

(*i*) (0.3, 0.4) when $2<n\leqslant 8$; and

(*ii*) (0.2, 0.3) when $8<n\leqslant 55$.

Lastly, we try to find upto what value of n (>55) the root of (1) will be between $x=.1$ and $x=.2$. Here we have to determine the value of n upto which

$$10[1-(\tfrac{1}{9}+\tfrac{1}{19}+{}^{1}+\ldots \text{ to } n \text{ terms})] \tag{3}$$

will remain positive. The series in ( ) is a divergent series but a slowly divergent one. This makes the actual summation process very tedious. To avoid this we take the help of the convergent sequence (u_n) defined by

$$u_n = 1+\tfrac{1}{2}+\tfrac{1}{3}+\ldots\ldots+\tfrac{1}{n}-\log n.$$

It is known that $0<u_n<1$, that (u_n) is a descending sequence and that its limit is the Euler's constant, γ, whose value is known to be $0.57721566\ldots$. We can therefore put

$$1+\tfrac{1}{2}+\tfrac{1}{3}+\ldots\ldots+\tfrac{1}{n}=\log n+\gamma+\varepsilon \tag{4}$$

where ε is a positive number tending to zero when n tends to infinity.

We have

$$(\tfrac{1}{9}+\tfrac{1}{19}+\ldots \text{ to } n \text{ terms}) > \tfrac{1}{10}\,(1+\tfrac{1}{2}+\ldots+\tfrac{1}{n})$$

$$\text{or, } > \tfrac{1}{10}\,(\log n+\gamma+\varepsilon).$$

The series on the left-hand side will surely exceed 1, if $\log n+\gamma+\varepsilon \geqslant 10$, or, $\log n \geqslant 9{\cdot}4227843\ldots$ neglecting ε for the time being. This leads to $n > 12367$ to the nearest integer. Again for $a > 0$,

$$\frac{1}{a+9} < \tfrac{1}{2}\left(\frac{1}{a+5}+\frac{1}{a+10}\right). \tag{5}$$

Putting $a=0, 10, 20\ldots$ in succession and summing upto n terms we get

$$(\tfrac{1}{9}+\tfrac{1}{19}+\ldots \text{to } n \text{ terms}) < \tfrac{1}{10}\,(1+\tfrac{1}{2}+\ldots\ldots+\tfrac{1}{n})$$

$$\text{or, } < \tfrac{1}{10}\,(\log 2n+\gamma+\varepsilon);$$

the series on the left-hand side will certainly be less than 1 if $\log 2n+\gamma+\varepsilon \leqslant 10$. Neglecting ε, as before, we get $n \leqslant 6184$ to the nearest integer. It will be our next endeavour to narrow down the limits for n by a considerable extent.

Although the value of γ has been calculated to several decimal places, I have not been able to find any reference as to the manner in which ε approaches zero. The value of ε in the neighbourhood of $n=10{,}000$ is specially needed here. I have therefore been obliged to calculate the values of ε for a series of increasing values of n, and the results are arranged in the following table.

TABLE I

Serial No.	n	$1+\frac{1}{2}+\dots+\frac{1}{n}$	ε	$\varepsilon \times n/110$
1	50	4.499 2052	0.0099 656	0.0045 298
2	110	5.282 2373	.0045 413	.0045 413
3	220	5.973 1177	.0022 745	.0045 490
4	330	6.377 8262	.0015 280	.0045 840
5	440	6.665 1277	.0011 373	.0045 492
6	550	6.888 0454	.0009 176	.0045 880
7	660	7.070 2170	.0007 617	.0045 702
8	770	7.224 2597	.0006 536	.0045 752
9	880	7.357 7103	.0005 727	.0045 816
10	990	7.475 4293	.0005 087	.0045 783
11	1100	7.580 7377	.0004 566	.0045 660
12	1210	7.676 0072	.0004 159	.0005 749
13	2400	8.360 6487	.0002 092	.0045 644
14	3700	8.793 4422	.0001 386	.0046 618

The above gives reliable results upto 5 decimals ; the last two figures are to be regarded as estimates towards further approximation.

The last column of the table gives an interesting result. It shows that ε varies *almost* inversely as n. I have used these data in drawing an ε -n curve, and from this trend-line I have tried to form an estimate of ε for $n=10{,}000$ or thereabouts. I realize that 10,000 is far removed from the last figure, *viz.*, 3,700, of the Table, but still the result of the last column makes me feel that I am not far from the true value when I estimate ε that will be about $0.0^4\,5$, or $(\gamma+\varepsilon)$ will be .577266 upto six decimals.

We now return to our problem. The sum of the series ($\frac{1}{9}+\frac{1}{19}+\dots$ to 1,200 terms), is found to be 0.7845335. Now, $\frac{1}{9}+\frac{1}{19}+\dots$ to n_1 terms

$$=\left(\frac{1}{9}+\frac{1}{19}+\dots+\frac{1}{11999}\right)+\left\{\frac{1}{12009}+\frac{1}{12019}+\dots \text{ to } (n_1-1200) \text{ terms}\right\}$$

$$>\left(\frac{1}{9}+\frac{1}{19}+\dots+\frac{1}{11999}\right)+\frac{1}{10}\left(1+\frac{1}{2}+\dots+\text{ to } n_1 \text{ terms}\right)$$
$$-\frac{1}{10}\left(1+\frac{1}{2}+\dots+\frac{1}{1200}\right),$$

or, $>0{\cdot}784\,5335+\frac{1}{10}(\log n_1+\gamma+\varepsilon)-0{\cdot}766\,7712.$

Let n_1 be such that the right-hand side $=1$; that is,

$$\log n_1+\gamma+\varepsilon=9.822377. \qquad (6)$$

Then the series (3) will be negative when $n \geqslant n_1$.

Again, with the help of (5) we have $\frac{1}{9} + \frac{1}{19} + \dots$ to n_2 terms

$$< \left(\frac{1}{9} + \frac{1}{19} + \dots + \frac{1}{11999}\right) + \frac{1}{2}\left\{\frac{1}{12005} + \frac{1}{12010} + \frac{1}{12015} + \frac{1}{12020} + \dots \text{ to } (2n_2 - 2400) \text{ terms}\right\},$$

$$\text{or, } < \left(\frac{1}{9} + \frac{1}{19} + \dots + \frac{1}{11999}\right) + \frac{1}{10}\left(1 + \frac{1}{2} + \dots \text{ to } 2n_2 \text{ terms}\right) - \frac{1}{10}\left(1 + \frac{1}{2} + \dots \text{ to } 2400 \text{ terms}\right)$$

$$\text{or, } < 0.7845335 + \frac{1}{10}(\log 2n_2 + \gamma + \varepsilon) - 0.8360649.$$

By putting the right-hand side $=1$, we get

$$\log 2n_2 + \gamma + \varepsilon = 10{\cdot}515314. \tag{7}$$

And the series will be positive when $n \leqslant n_2$.

Subtracting (6) from (7) we get

$$\log \frac{2n_2}{n_1} = .692937 \text{ nearly,}$$

$$\text{whence } \frac{2n_2}{n_1} = 1.99958.$$

Therefore, $\frac{n_2}{n_1} = .99979$, or, $\frac{9998}{10000}$ approximately.

If the n's are in the neighbourhood of 10,000, then $n_1 - n_2 = 2$. Since the required value of n satisfies the condition $n_2 < n < n_1$, it is evident that we must have

$$n = n_1 - 1 = n_2 + 1.$$

If we put $(\gamma + \varepsilon) = 0\ 577266$ in (6) and (7), we get $n_1 = 10354$, and $n_2 = 10352$ upto the nearest integers. Hence we arrive at the result that the maximum ordinate of $F_n(x)$ will lie in the range (0.1, 0.2) when $55 < n \leqslant 10353$.

It is then evident that for $n \geqslant 10354$, the maximum ordinate will correspond to values of x lying between $x=0$ and $x=\cdot 1$.

(*iii*) Let us now search for the smallest of the maximum ordinates of $F_n(x)$ when n is even and $=2m$. It follows from the symmetry of the graph about the point $x=m$ that there are two corresponding values of x in this case, one in the interval $(m-1, m)$ and the other in $(m, m+1)$. In order to locate the latter it is convenient first to change the origin to $x=m$. Put $x=x'+m$; then we have to determine the maximum ordinate of $F_{2m}(x'+m)$ when x' lies between 0 and 1. We have here

$$\frac{1}{F_{2m}}\frac{dF_{2m}}{dx} = \frac{1}{x'} - 2x'\left\{\frac{1}{1^2 - x'^2} + \frac{1}{2^2 - x'^2} + \dots + \frac{1}{m^2 - x'^2}\right\}. \tag{8}$$

We know that the series

$$\frac{1}{x'} - 2x'\left\{\frac{1}{1^2 - x'^2} + \frac{1}{2^2 - x'^2} \dots \text{ to } \infty\right\} = \pi \cot \pi x'.$$

Therefore, when $x' = \frac{1}{2}$, this series has zero for its sum, whence it follows that

$$\frac{1}{1^2 - \frac{1}{4}} + \frac{1}{2^2 - \frac{1}{4}} + \dots + \frac{1}{m^2 - \frac{1}{4}} < 2.$$

Therefore, the right-hand side of (8) is positive for $x'=\frac{1}{2}$. This can be seen to be a negative quantity, for $m>1$ and $x'=0.6$. Hence this changes sign as x' increases from 0.5 to 0.6. The smallest of the maximum ordinates of $F_{2m}(x)$ lies therefore in the range $(m+0.5, m+0.6)$.

(*iv*) *Asymptotic expressions when n is very large.*

$$F_{2m}(x'+m)=(-1)^m (m!)^2 .\ x'\left(1-\frac{x'^2}{1^2}\right)\left(1-\frac{x'^2}{2^2}\right)\cdots\left(1-\frac{x'^2}{m^2}\right).$$

Therefore when m is very large, we have by Stirling's theorem,

$$F_{2m}(x'+m)\backsim(-1)^m .\ 2e^{-2m} .\ m^{2m+1}\sin\pi x'.$$

Hence the least of the maximum ordinates $\backsim(-1)^m .\ 2e^{-2m} .\ m^{2m+1}$ since $x'\rightarrow\frac{1}{2}$ for the maximum value when $m\rightarrow\infty$. The above expression becomes

$$(-1)^{n/2} .\ 2e^{-n} .\ \left(\frac{n}{2}\right)^{n+1} \tag{9}$$

in terms of n. And it is easy to see that the value of the least maximum ordinate when n is odd is also equivalent to this expression when n is very large, except for the first factor which becomes $(-1)^{\frac{n+1}{2}}$.

We have seen that the root of $F_n'(x)=0$, which lies between 0 and 1, tends to zero when $n\rightarrow\infty$, and that this tending to zero is as slow as that of the infinite series $\Sigma\frac{1}{n}$. For approximate purposes we can thus put the root to be equal to λ/n, when n is very large, λ being some finite quantity. Hence an estimate of the greatest maximum ordinate of $F_n(x)$ will be

$$F\left(\frac{\lambda}{n}\right)\backsim(-1)^n\lambda(n-1)!\backsim(-1)^n\lambda\sqrt{2\pi} .\ n^{n-\frac{1}{2}}e^{-n}, \tag{10}$$

by Stirling's theorem. Therefore, for very large n, an estimate of the ratio

$$\left|\frac{\text{greatest max.}}{\text{least max.}}\right|=\frac{\lambda\sqrt{2\pi} .\ 2^n}{n^{3/2}}, \tag{11}$$

a quantity which is very large and tends to infinity with n.

The area under the curve $y=F_n(x)$ in the interval $(0, 1)$ is intermediate in value between the area of the triangle on the x-axis, whose vertex is the point of maximum ordinate, and the area of the trapezium whose three sides are the tangents to the curve at $x=0$, at the point of maximum ordinate and at $x=1$. That is, $\frac{1}{2}m_n <$ area under the curve

$$<\frac{1}{2}m_n\left[2-\left\{\frac{1}{|F_n'(0)|}+\frac{1}{|F_n'(1)|}\right\}m_n\right],$$

where m_n represents the magnitude of the maximum ordinate; or, $\frac{1}{2}m_n <$ area under the curve $<\frac{1}{2}m_n\left[2-\frac{n+1}{n}m_n\right]$.

Therefore, $\frac{n+1}{n!} m_n < 1$, or, $m_n < \frac{n!}{n+1} < (n-1)!$. Comparing this with (10), we see that $|\lambda| < 1$.

Further, if λ depends on n so that we may write it as $\lambda(n)$, it will appear from (15) and (17a) that we must have

$$\underset{n \to \infty}{\text{Lt.}} \frac{\lambda(n+1)}{\lambda(n)} = 1.$$

(v) I have calculated the approximate magnitudes of the maximum ordinates of $F_n(x)$ upto $n = 10$, and the results are arranged in the following Table.

TABLE II

n	No. of diff. max. ordinates	Corres. Values of x	Magnitudes of the max. ordinates	Ratios to the least max.	Success. ratios of the max.
1	One	0.5	0.25	..	..
2	One	0.42265	0.3849	..	..
3	Two	0.374 1.5	0.9997 0.5625	1.79	1.79
4	Two	0.351 1.456	3.631 1.4186	2.55	2.55
5	Three	0.3341 1.4258 2.5	16.8973 5.0489 3.515	4.80 1.44	3.34 1.44
6	Three	0.321 1.4043 2.469	95.8413 23.149 12.3587	7.75 1.87	4.14 1.87
7	Four	0.310 1.3867 2.4452 3.5	640.601 129.738 56.1371 43.0664	14.88 3.01 1.30	4.94 2.31 1.30
8	Four	0.3006 1.3716 2.4272 3.4765	4929.2 858.88 312.298 194.307	25.37 4.42 1.61	5.74 2.75 1.61
9	Five	0.2923 1.3567 2.4124 3.4567 4.5	49200.9 6555.68 2059.62 1075.1 872.1	49.19 7.51 2.36 1.23	6.86 3.18 1.91 1.23
10	Five	0.2848 1.3467 2.3998 3.441 4.4809	416613.3 56661.98 15604.5 7042.31 4804.87	86.70 11.79 3.25 1.47	7.35 3.63 2.21 1.47

9. ***Ratio of the greatest to the least magnitudes of maximum ordinates of*** **$F_n(x)$.**—From a study of the last two columns of Table II it will appear that the ratio of the greatest to the least of the maximum increases quite rapidly as n increases, and that the successive ratios all increase with n. Let us put

$$P_n = \frac{|\text{greatest max. of } F_n(x)|}{|\text{least max. of } F_n(x)|}$$

(*i*) Let n be odd, $=2m+1$, and let $|F_{2m+1}(\xi)|$ and $|F_{2m-1}(\xi')|$ be the greatest *magnitudes* of the maximum ordinates of the two functions $F_{2m+1}(x)$ and $F_{2m-1}(x)$. Then it is evident from (3) that $\xi<\xi'$. Each is less than .3 when $m \geqslant 5$, less than .2 when $m \geqslant 28$, and less than .1 when $m \geqslant 5177$. We shall have

$$\frac{P_{2m+1}}{P_{2m-1}} = \frac{4}{(2m+1)^2}\,\frac{(2m+1-\xi')(2m-\xi')\,|F_{2m+1}(\xi)|}{|F_{2m+1}(\xi')|}.$$

$$> \frac{4\,\{4m^2+(1-2\xi').2m-\xi'(1-\xi')\}}{(2m+1)^2}$$

$$>4-\frac{2m(1+2\xi')+1+\xi'(1-\xi')}{m(m+1)} \tag{12}$$

When $m \geqslant 5$, $\xi'<.3$; and $\xi'(1-\xi')<0.25<2.2$. Therefore,

$$\frac{P_{2m+1}}{P_{2m-1}} > 4-\frac{3.2}{m} > 3.36. \tag{13}$$

Next, for $m \geqslant 28$, $\xi'<0.2$, and $\xi'(1-\xi')<1.8$.

Therefore, this ratio $>4-\frac{2.8}{m}$ or 3.9, for $m \geqslant 28$.

Finally for $m \geqslant 5177$, $\xi'<.1$ and $\xi'(1-\xi')<1.4$.

Therefore, the ratio $>4-\frac{2.4}{m}$ or 3.99954.

Again, we can put

$$\frac{P_{2m+1}}{P_{2m-1}} = \frac{4}{(2m+1)^2}\cdot\frac{(2m+1-\xi)\ (2m-\xi)\ |F_{2m-1}(\xi)|}{|F_{2m\ 1}(\xi')|}$$

$$< \frac{4}{(2m+1)^2}\,(2m+1-\xi)\ (2m-\xi).$$

The right-hand side is obviously $<\frac{8m}{2m+1}<4$. Combining this with (13) we get

$$4-\frac{3.2}{m} < \frac{P_{2m+1}}{P_{2m-1}} < 4. \tag{14}$$

This shows that when $m \longrightarrow \infty$, $\dfrac{P_{2m+1}}{P_{2m-1}} \longrightarrow 4$, (15)

[*Cf.* (11)].

(*ii*) Let n be even, $=2m$, and let $| F_{2m}(\xi) |$ and $| F_{2m-2}(\xi') |$ be the greatest magnitudes of the maximum ordinates of the two functions $F_{2m}(x)$ and $F_{2m-2}(x)$. Then ξ and ξ' will satisfy similar conditions as before. Further, let $| F_{2m}(m+\zeta) |$ and $| F_{2m-2}(m-1+\zeta') |$ be the least magnitudes of the maximum ordinates of the two functions respectively. Then $\zeta<\zeta'$, and both lie between 0.5 and 0.6, as has been proved before.

$$\frac{P_{2m}}{P_{2m-2}}=\frac{(2m-\xi')(2m-1-\xi')|F_{2m}(\xi)||F_{2m-2}(m-1+\zeta')}{F_{2m}(\xi')|(m^2-\zeta^2)|F_{2m-2}\cdot(m-1+\zeta)|}.$$

$$>\frac{(2m-\xi')(2m-1-\xi')}{m^2-\zeta^2}>\frac{(2m-.3)(2m-1.3)}{m^2-\frac{1}{4}},$$

by replacing ξ' by .3 and ζ by $\frac{1}{2}$. Thus the ratio $>\frac{4m^2-3.2m}{m^2}$,

or, $4-\frac{3.2}{m}>3.46$, if $m \geqslant 6$.

In the same way, it can be shown that the ratio will exceed 3.9 for $m \geqslant 29$ and 3.99934 for $m \geqslant 5178$. Again since

$$\frac{P_{2m}}{P_{2m-2}}=\frac{(2m-\xi)(2m-1-\xi)|F_{2m-2}(\xi)||F_{2m}(m+\zeta')|}{|F_{2m-2}(\xi')|(m^2-\zeta'^2)|F_{2m}(m+\zeta)|},$$

$$<\frac{(2m-\xi)(2m-1-\xi)}{m^2-\zeta^2}<\frac{2m(2m-1)}{m^2}<4.$$

Hence we see that this ratio too is subject to the same restrictions, *viz.*, (14) and (15), as $\frac{P_{2m+1}}{P_{2m-1}}$.

(*iii*) If we consider the ratio of the consecutive P's, *viz.*, P_{2m+1}/P_{2m}, it can be shown that

$$\frac{P_{2m+1}}{P_{2m}}>\frac{2m+.7}{m+\frac{1}{2}}, \text{ or } 2-\frac{0.3}{m+\frac{1}{2}}>2-\frac{0.3}{m}. \tag{16}$$

For $m \geqslant 5$ the ratio is seen to be greater than 1.94. This ratio is also

$$<\frac{2m+1}{m+.4}, \text{ or } 2+\frac{0.2}{m+.4}>2+\frac{1}{5m}. \tag{17}$$

Thus,

$$2+\frac{1}{5m}>\frac{P_{2m+1}}{P_{2m}}>2-\frac{2.3}{m}. \tag{17a}$$

Similarly one can show that

$$2-\frac{2}{2m+1}>\frac{P_{2m}}{P_{2m-1}}>2-\frac{3}{2m}. \tag{17b}$$

Hence, when $m \longrightarrow \infty$, the ratio tends to 2 [*Cf.* (11)].

(*To be continued*)

RAJARAM COLLEGE,
KOLHAPUR

DETERMINATION OF THE SPACE GROUPS OF THE CRYSTALS OF DIPHENYL-BENZAMIDE AND ANISIC ACID

By

R. K. Rokade, R. H. Khabaria and M. R. Kapadia

Abstract

CRYSTALS of Diphenyl-Benzamide and Anisic acid have been studied by the rotating crystal method. The dimensions of the unit cell, the number of molecules in the cell and the space groups to which the crystals belong are determined.

(A) Diphenyl-Benzamide

The crystals of Diphenyl-Benzamide develop *c*(001), *a*(100), *p*(110), *b*(010) and *e*(011) faces. The crystals belong to the rhombic class and the axial ratio is

$$a : b : c = 0.9501 : 1 : 0.324.$$

(*cf.* Groth, Chem. Kristallg., V, p. 305).

In this investigation, the crystals of Diphenyl-Benzamide were prepared by the slow evaporation of the solution of the substance in absolute ethyl alcohol. Rotation and oscillation photographs were taken about *a*, *b*, and *c* axes using *Cu*, *K*-radiation.

The lengths of the axes as determined from rotation photographs (Plates, I, II and III) are $a=17.65$A°, $b=9.060$ A° and $c=17.96$ A°. The axial ratio, therefore, is $a : b : c = 1.953 : 1 : 1.983$. The ratio $a : b$ is doubled and $c : b$ is six times as that given in Groth (*loc. cit.*). The number of molecules in the unit cell as calculated from the above values and the specific gravity of the crystals 1.273 determined by the floatation method is nearly 8 (exactly 8.067). The indices of the planes appearing in the various oscillation photographs were obtained by the aid of Bernal's Chart. The intensities of the planes were determined by eye estimation and the symbols used have the usual meaning. The list of planes observed is given in Tables I and II.

TABLE I

Axial Planes	Prism Planes (okl)	Prism Planes (hol)	Prism Planes (hko)
002 v.s.	021 s.	102 m.s.	210 v.s.
004 m.s.	022 s.	104 m.	220 v.s.
006 m.s.	023 m.	106 w.	230 m.s.
008 m.s.	024 s.	202 m.s.	240 m.
020 v.s.	025 s.	204 m.	250 w.
400 m.s.	026 w.	206 m.	410 m.s.
200 v.s.	041 w.	302 m.	420 s.
400 m.s.	042 m.	304 s.	430 m.
600 m.	043 m.	306 w.	440 m.s.
800 w.m.	044 w.	308 m.	450 v.w.
......	045 v.w.	402 s.	610 s.
......	......	406 w.	620 w.
......	......	502 s.	630 m.s.
......	......	506 s.	810 m.
......	......	602 m.s.	......
......	.....	604 s.	......
......	......	704 m.s.	......

TABLE II

General Planes

111 w.m.	211 m.	311 w.	411 m.	611 m.s.	711 v.w.
112 w.m.	212 m.	312 v.s.	412 s.	613 m.s.	712 w.m.
113 s.	214 m.	313 m.s.	413 m.s.	616 m s.	716 v.w.
114 v.s.	215 v.w.	316 v.w.	414 s.	621 s.	722 m.s.
116 m.	216 w.m.	318 m.	416 m.	622 v.s.	726 v.w.
117 m.	217 v.w.	321 v.w.	418 w.m.	623 m.	727 v.w.
118 m.	221 s.	322 m.	421 s.	626 v.w	811 v.w.
121 m.	222 s.	323 m.s.	422 m.s.	627 w.	812 v.w.
122 m.s.	223 s.	324 v.w.	431 w.m.	631 m.	814 w.
123 s.	224 m.s.	325 v.w.	432 m.s.	633 v.w.	821 v.w.

TABLE II—*contd.*

124 m.s.	225 v.w.	326 v.w.	433 w.m.	635 v.w.	831 v.w.
125 m.s.	226 v.w.	327 v.w.	441 w.m.	636 v.w.	911 v.w.
126 w.	231 m.s.	333 m.	511 m.s.	641 v.w.	912 v.w.
127 w.	232 s.	342 w.	512 m.s.	......	914 w.
131 w.	233 m.	343 w.m.	513 m.s.	......	......
133 w.m.	234 m.	346 w.m.	514 v.w.	......	......
136 v.w.	235 v.w.	......	515 m.	......	......
137 v.w.	241 v.w.	......	516 v.w.	......	......
141 w.	242 v.w.	......	517 w.	......	......
142 m.	243 v.w.	......	521 s.	......	......
144 m.	244 v.w.	......	522 m.	......	......
145 w.	245 w.m.	......	533 m.	......	......
......	246 w.m.	......	534 v.w.	......	......
......	......	......	541 w.	......	......
......	......	......	544 v.w.	......	......

It will be seen from the list of planes that (*hol*) planes are halved when l is odd, (*okl*) planes are halved when k is odd and (*hko*) planes are halved when h is odd. There are no halvings in the general planes. These halvings assign the crystals of Diphenyl-Benzamide to the space group $\underline{Qh}^{15}$ of the rhombic bipyramidal class. (*cf.* Astbury and Yardley, Phil. Trans., 1924, A, 224, 235). The number of molecules required by the space group is 8. Thus the molecules of Diphenyl-Benzamide are asymmetric.

(B) ANISIC ACID

The crystals of anisic acid develop *a* (100), *b*(010), *c*(001), *m*(110) and *o*(111) faces. The crystals belong to the monoclinic prismatic class and the axial ratio is $a : b : c = 1.5497 : 1 : 0.3615$; $\beta = 98°26'$. (*cf.* Groth, Chem. Kristallg., IV, p. 504). In this investigation the crystals of anisic acid were prepared by the slow evaporation of the solution of the substance in absolute alcohol. Rotation and oscillation photographs were taken about *a*, *b* and *c* axes using *Cu*, *K*-radiation. The lengths of the axes as determined from the rotation photographs (Plates, IV, V and VI) are $a = 16.94$ A°, $b = 10.94$ A° and $c = 3.953$ A°. The axial ratio, therefore, is $a : b : c = 1.548 : 1 : 0.3614$. This agrees well with that given in Groth (*loc. cit.*). The number of molecules in the unit cell as calculated from the above values and the specific gravity (1.385) of the crystals determined by the floatation method is nearly 4 (exactly 3.978). The indices and intensities of the planes appearing in various oscillation photographs are obtained as in the case of the crystals of Diphenyl-Benzamide. The list of planes observed is given in Tables III and IV.

TABLE III

Axial Planes	Prism Planes (hol)	Prism Planes (okl)	Prism Planes (hko)
002 s.	$10\bar{1}$ v.s.	011 s.	110 s.
020 s.	101 v.s.	012 w.	120 v.s.
040 m.s.	$20\bar{2}$ m.s.	021 v.w.	130 m.s.
060 w.	202 m.	022 w.m.	140 m.s.
200 v.s.	$30\bar{1}$ s.	031 w.	150 m.s.
600 m.	301 w.	032 v.w.	210 v.s.
800 w.	$40\bar{2}$ w.m.	041 m.	220 m.s.
....	501 w.m.	051 v.w.	230 m.s.
....	$70\bar{1}$ m.	....	240 m.
....	701 m.	....	250 m.s.
....	$90\bar{1}$ m.s.	....	320 m.s.
....	....	....	340 m.s.
....	....	....	350 m.
....	....	....	410 w.m.
....	....	....	420 m.s.
....	....	....	430 m.s.
....	....	....	440 s.
....	....	....	450 m.
....	....	....	510 s.
....	....	....	520 m.
....	....	....	530 m.s.
....	....	....	540 s.
....	....	....	550 m.s.
....	....	....	610 v.w.
....	....	....	620 s.
....	....	....	640 w.m.
....	....	....	710 s.
....	....	....	720 w.m.
....	....	....	730 v.w
....	....	....	810 w.m.
....	....	....	820 w.
....	....	....	910 v.w.

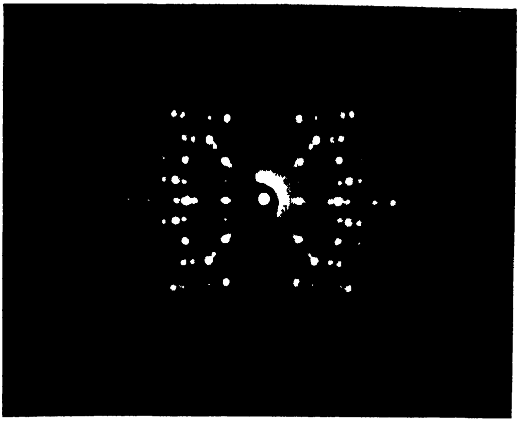


Plate I. a Axis

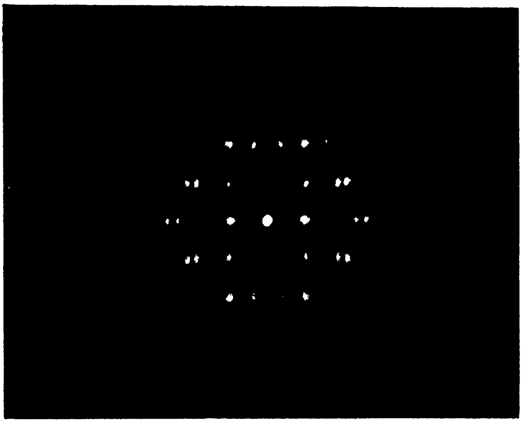


Plate II. b Axis

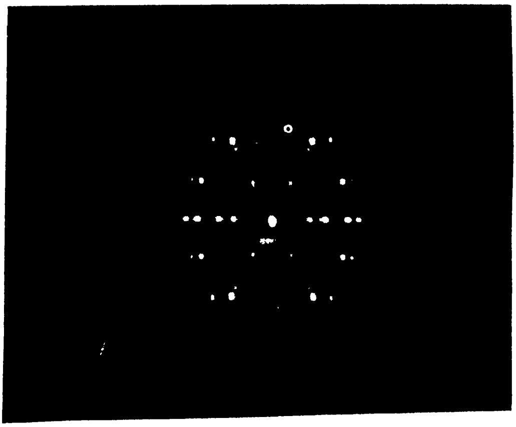


Plate III. c Axis

ROTATION PHOTOGRAPHS OF DIPHENYL BENZAMIDE

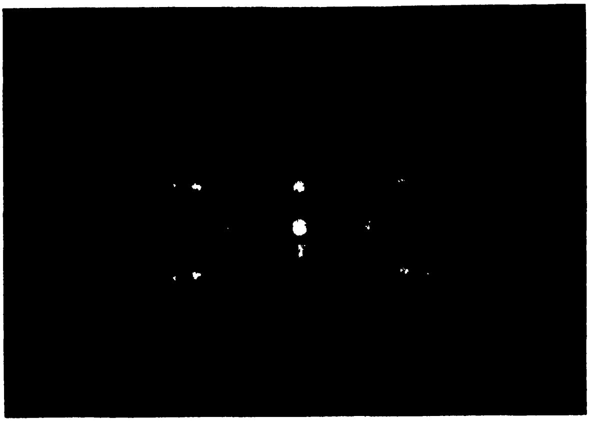


Plate IV. a Axis

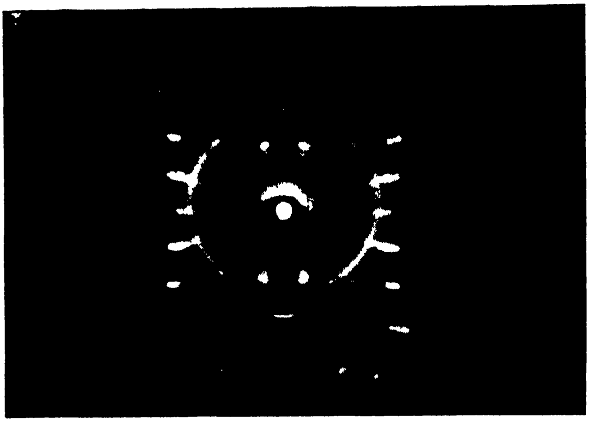


Plate V. b Axis

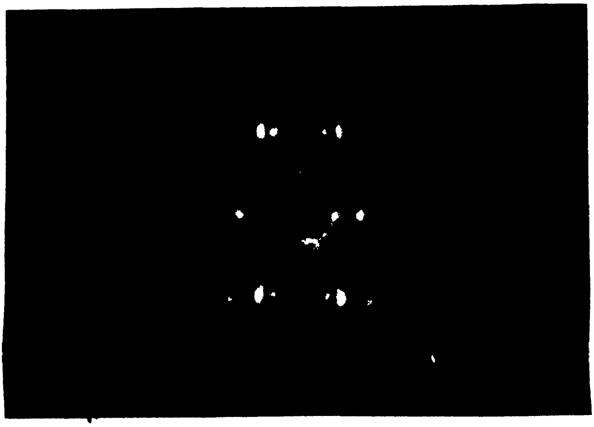


Plate VI. c Axis

ROTATION PHOTOGRAPHS OF ANISIC ACID

Table IV

General Planes

$11\bar{1}$ v.s.	$31\bar{1}$ m.s.	$51\bar{1}$ w.m.	$71\bar{1}$ s.
111 v.s.	311 s.	511 w.m.	711 w.m.
112 m.	312 v.w.	$52\bar{1}$ w.	$72\bar{1}$ w.
$12\bar{1}$ s.	$32\bar{1}$ m.s.	521 v.w.	721 w.
$12\bar{2}$ m.	321 m.	$53\bar{1}$ v.w.	$73\bar{1}$ w.
121 w.	322 w.m.	$53\bar{2}$ w.m.	731 w.m.
122 m.s.	$33\bar{1}$ w m.	531 w.	$74\bar{1}$ v.w.
$13\bar{1}$ s.	331 w.m.	$54\bar{1}$ m.	$81\bar{1}$ v.w.
131 m.s.	332 w.	541 w.m.	811 v.w.
$14\bar{1}$ m.s.	$34\bar{1}$ w.	551 m.	$82\bar{1}$ v.w.
141 m.	341 v.w.	$61\bar{1}$ v.s.	$83\bar{1}$ v. w.
$15\bar{1}$ v.w.	$35\bar{1}$ w.	611 m.s.	$91\bar{1}$ v.w.
151 w.m.	351 v.w.	$62\bar{1}$ w.m.	$92\bar{1}$ v.w.
$21\bar{1}$ m.s.	$41\bar{1}$ m.	621 v.w.	....
$21\bar{2}$ m.s.	$41\bar{2}$ m.	$63\bar{1}$ w.	....
211 s.	411 w.m.	631 w.	....
212 m.s.	412 m.	$64\bar{1}$ m.s.	....
$22\bar{1}$ s.	$42\bar{1}$ w.m.	641 m.	....
$22\bar{2}$ m.	421 v.w.	....	....
221 s.	422 v.w.	....	....
222 m.	$43\bar{1}$ m.	....	....
$23\bar{1}$ m.	431 w.m.	....	....
231 m.s.	432 v.w.	....	....
232 w.m.	$44\bar{1}$ w.	....	....
$24\bar{1}$ m.s.	441 v.w.	....	....
241 v.w.	$45\bar{1}$ w.m.	....	....
$25\bar{1}$ v.w.	451 v.w.	....	....
251 w.	....	....	...

It will be seen from the list of planes that (*hol*) planes are halved when ($h+l$) is odd, and (010) is also halved. These halvings assign the crystals of anisic acid to the space group $C^{5}h$. (*cf.* Astbury and Yardley, Phil. Trans., 1924, A, 224, 230). The number of molecules required by the space group is four. Thus the molecules of anisic acid are asymmetric.

In accordance with the observed halvings there will be a molecule situated at the centre of the *a*—*c* face. This arrangement is usually disallowed in the monoclinic and triclinic crystals. It is, therefore, necessary to determine a new set of axes to define the true unit cell. The relation between the crystallographic and the true unit cells is obtained as in the case of the crystals of *p*-Aminobenzoic acid. (*cf.* J. Bom. Univ., Vol. VIII, Part 3, Nov. 1939).

The dimensions of the true unit cell are :—

$$a = 16.82\text{A}^\circ,\ b = 10.94\text{A}^\circ,\ c = 3.953\text{A}^\circ,\ \beta = 94^\circ\ 54'.$$

This gives the axial ratio to be 1.538 : 1 : 0.3614.

The planes observed in the oscillation photographs about the crystallographic *a*, *b* and *c* axes have been converted with reference to the new axes and are shown in Tables V and VI.

TABLE V

Axial Planes	Prism Planes (hol)	Prism Planes (okl)	Prism Planes (hko)
001 v.s.	$20\bar{1}$ s.	011 v.s.	110 s.
002 m.s.	$20\bar{2}$ s.	012 m.s.	120 v.s.
020 v.s.	201 s.	021 s.	130 m.s.
040 m.s.	202 w.m.	022 m.	140 m.s.
060 w.	$40\bar{1}$ w.	031 s.	150 m.s.
200 v.s.	$40\bar{2}$ m.	041 m.s.	210 v.s.
600 m.	$60\bar{1}$ w.m.	051 v.w.	220 m.s.
800 w.	601 m.	....	230 m.s.
....	$80\bar{1}$ m.	....	240 m.
....	801 m.s.	....	250 m.s.
....	....	....	320 m.s.
....	....	....	340 m.s.
....	....	....	350 m.
....	....	....	410 w.m.
....	....	..	420 m.s.
....	....	....	430 m.s.
....	....	...	440 s.

TABLE V—*contd.*

Axial Planes	Prism Planes (hol)	Prism Planes (okl)	Prism Planes (hko)
....	....	....	450 m.
....	....	....	510 s.
....	....	....	520 m.s.
....	....	....	530 m.s.
....	....	....	540 s.
....	....	....	550 m.s.
....	....	....	610 v.w.
....	....	....	620 s.
....	....	....	640 w.m.
....	....	....	710 s.
....	....	....	720 w.m.
....	....	....	730 v.w.
....	....	....	810 w.m.
....	....	....	820 w.
....	....	...	910 v.w.

TABLE VI

General Planes

$11\bar{1}$ s.	$31\bar{1}$ s.	$51\bar{1}$ w.m.	$71\bar{1}$ m.s.
111 m.s.	$31\bar{2}$ m.	$51\bar{2}$ v.w.	711 v.w.
$12\bar{1}$ v.w.	311 m.	511 v.s.	$72\bar{1}$ w.
$12\bar{2}$ m.	$32\bar{1}$ s.	$52\bar{1}$ v.w.	721 v.w.
121 s.	$32\bar{2}$ m.s.	$52\bar{2}$ w.m.	$73\bar{1}$ v.w.
$13\bar{1}$ w.	321 w.m.	521 w.m.	731 v.w.
131 m.	$33\bar{1}$ m.s.	$53\bar{1}$ w.m.	$74\bar{1}$ m.
$14\bar{1}$ m.	331 m.	$53\bar{2}$ w.	$81\bar{1}$ w.m.
141 m.s.	332 w.m.	531 w.	811 v.w.
$15\bar{1}$ v.w.	$34\bar{1}$ v.w.	$54\bar{1}$ v.w.	$82\bar{1}$ w.
151 v.w.	341 w.	541 m.s.	821 v.w.

TABLE VI—*contd.*

$21\bar{1}$ v.s.	$35\bar{1}$ w.	$55\bar{1}$ v.w.	$83\bar{1}$ w.m.
$21\bar{2}$ w.	351 w.m.	$61\bar{1}$ w.m.	$91\bar{1}$ v.w.
211 m.s.	$41\bar{1}$ s.	$61\bar{2}$ m.	....
212 m.	$41\bar{2}$ m.s.	611 s.	....
$22\bar{1}$ w.	411 w.m.	$62\bar{1}$ v.w.	....
$22\bar{2}$ w.m.	$42\bar{1}$ m.	$62\bar{2}$ v.w.	....
221 m.s.	$42\bar{2}$ m.	621 w.n.	....
$23\bar{1}$ m.s.	421 w.	$63\bar{1}$ w.	....
$23\bar{2}$ v.w.	$43\bar{1}$ w.m.	$63\bar{2}$ v.w.	....
231 w.m.	$43\bar{2}$ w.m.	631 w.	....
$24\bar{1}$ m.	431 v.w.	$64\bar{1}$ w.m.	....
241 w.	$44\bar{1}$ v.w.	641 v.w.	....
$25\bar{1}$ w.m.	441 m.	$65\bar{1}$ m.	....
251 w.	$45\bar{1}$ v.w.	....	....

It will be seen from these tables that the planes (*hol*) are halved when *h* is odd and the crystals belong to the same space group C_2^5h as obtained before. Further the number of molecules in the unit cell is 4.

The authors are thankful to Dr. Mata Prasad, D.Sc., F.I.C., for his guidance and help.

CHEMICAL LABORATORIES,
ROYAL INSTITUTE OF SCIENCE,
BOMBAY

[*Received : July 27, 1942*]

EFFECT OF METEOROLOGICAL CONDITIONS

On the Electrical Conductivity of Air at Colaba (Bombay)

By

S. M. MUKHERJEE, M.SC.

SUMMARY

DATA of electrical conductivity of the air at Colaba measured with a Gerdien apparatus during 1935-36 are correlated with the meteorological conditions prevailing at the time of observation. It is found that conductivity is much more dependent on wind direction during the dry months November to April than during the period May to October. This is explained as being due to the difference in the nature and concentration of pollution such as smoke, dust and products of combustion from the commercial and industrial parts of the city during the former period and sea spray and salt nuclei in the latter. When dust is raised in the air by wind, it increases the conductivity, the value being greater at a height of about 50 feet above ground than near it. Improvement of visibility goes hand in hand with increase of conductivity and *vice versa*. During rain, negative conductivity increases rapidly with intensity of rainfall but positive conductivity remains practically steady and somewhat below its normal value. The diurnal and seasonal variations of conductivity and visibility in Bombay are found to be similar. The conductivity is greater after than during rain. The best time of the day for regular daily observations of air conductivity at Colaba is discussed.

INTRODUCTION

Observations of electrical conductivity of air at the Colaba Observatory were carried out during 1935-36 with a Gerdien apparatus on the top floor of the balloon tower of the observatory which is 23 meters above ground and of area 3.3 m×3.1 m. A discussion of the diurnal and annual variation of the element during electrically quiet days has been already published[1]. In the present note, the values of conductivity are correlated with those of meteorological elements.

To explain the effect of wind on atmospheric electric conditions at the observatory, a sketch map of Colaba and its environs is useful and is given in Figure 1.

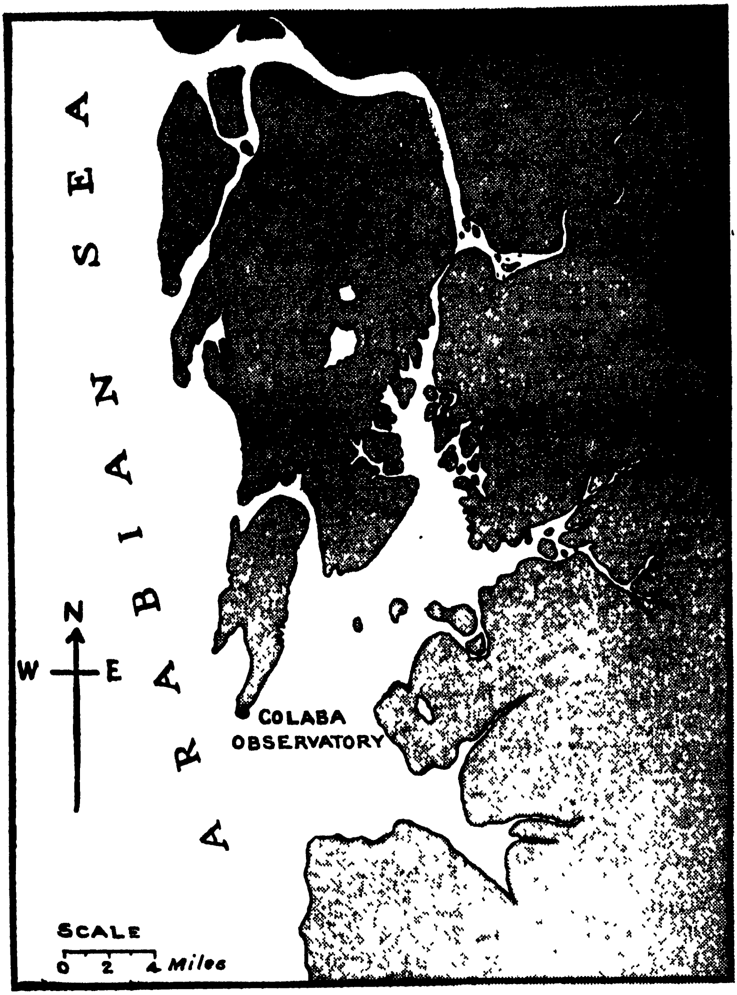


Fig. 1. Environs of Colaba Observatory

1. Effect of Wind.—For the purpose of this analysis, the year is divided into two periods—dry and humid. The dry period includes the months November to April and the humid period, May to October.

Data relating to changes of conductivity with wind direction are given in Tables 1 (*a*, *b*) and those with wind velocity in Tables 2 (*a*, *b*). The values given in the Tables are the means of those observed under the specified conditions. The numbers in the last row represent the total number of observations.

TABLE I

Variation of Conductivity with Wind Direction

(Unit of Conductivity $=10^{-4}$ E.S.U.)

(*a*) *Dry Period* (*November to April*)

Wind Direction	(1) NNE-E	(2) N and ESE-SSE	(3) S-NNW
Conductivity	0.81 0.83 1.64 0.98 546	1.14 1.14 2.28 1.00 172	1.45 1.56 3.01 0.93 670

(*b*) *Humid Period* (*May to October*)

Wind Direction	(1)	(2)	(3)
Conductivity	1.15 1.14 2.29 1.01 148	1.55 1.55 3.10 1.00 116	1.88 1.90 3.78 0.99 1312

TABLE II

Variation of Conductivity with Wind Speed

(Unit of Conductivity $=10^{-4}$ E.S.U.)

(*a*) *Dry Period* (*November to April*)

Wind Velocity (m.p.h.)	0—3	4—5	6—7	8—9	10—11	12—13	14—16
Conductivity	0.96 1.00 1.96 0.96 206	0.99 1.03 2.02 0.96 466	1.21 1.27 2.48 0.95 322	1.60 1.68 3.28 0.95 182	1.73 1.83 3.56 0.95 138	1.74 1.84 3.58 0.94 68	1.62 1.72 3.34 0.94 54

(*b*) *Humid Period* (*May to October*)

Wind Velocity (m.p.h.)	0—3	4—5	6—7	8—9	10—11	12—13	14—15	16—17	18—20
Conductivity	1.48 1.54 3.02 0.96 60	1.93 2.02 3.95 0.96 216	1.90 1.92 3.82 0.99 240	1.82 1.87 3.69 0.97 180	1.79 1.80 3.59 0.99 232	1.75 1.79 3.54 0.98 148	1.78 1.77 3.55 1.01 144	1.71 1.79 3.50 0.96 46	1.72 1.64 3.36 1.05 24

The changes of total conductivity with wind direction and velocity are shown in Figures 2 and 3 respectively. Curves A and B refer to the dry and humid periods respectively.

In Tables 1 (*a*) and (*b*) the data of conductivity have been grouped according to the sector from which the wind comes (1) NNE-E (City area), (2) N (Malabar Hill) and ESSE-SSE (Mainland) and (3) S-NNW (Sea). The directions N and ESE-SSE have been grouped together, because lands in those directions contain residential buildings, but no factories. It will be seen from both these Tables that the conductivity is least when the wind blows from the first quadrant, apparently because the air is then laden with the maximum concentration of pollution from the ships in the harbour and the industrial and commercial parts of the city, and the conductivity is greatest when the wind comes from the sea.

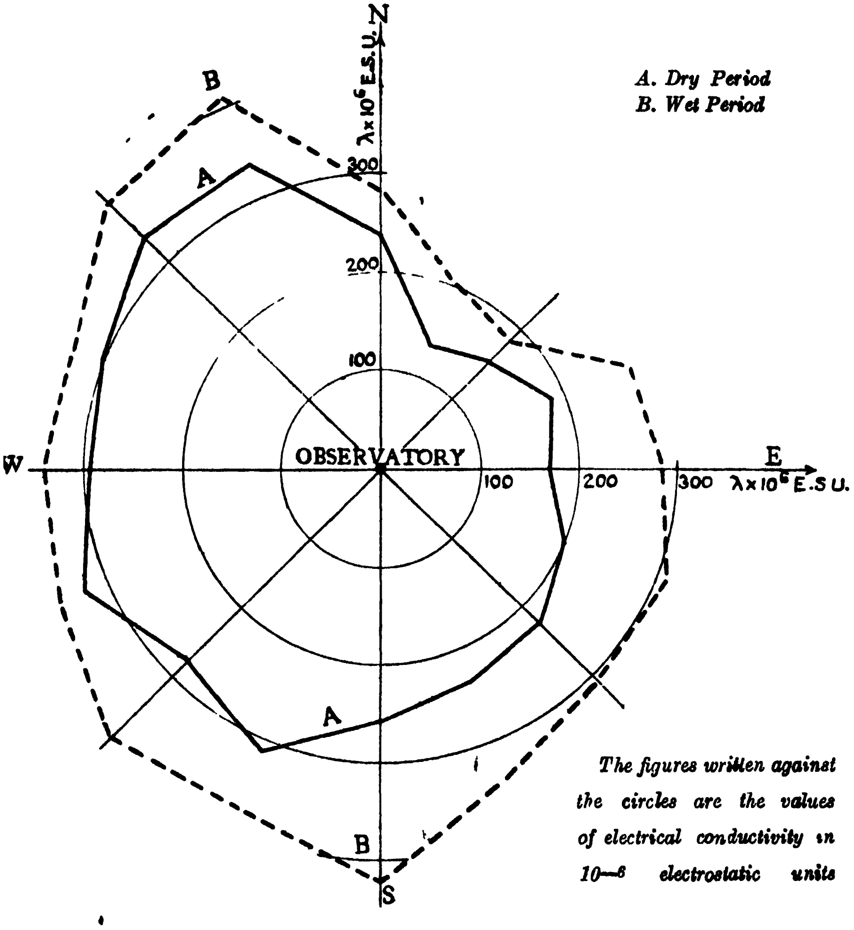


Fig. 2. Wind Direction and Electrical Conductivity of Air at Colaba

The dependence of conductivity on the wind direction is shown in Figure 2. It is clear from Figure 2 that the conductivity is generally smaller in the dry than in the wet months, irrespective of wind direction. This is due to the comparative purity of the air during the monsoon. The value corresponding to the N⟶E quadrant in the dry period is about 130% less than that corresponding to the S⟶W quadrant in the wet period.

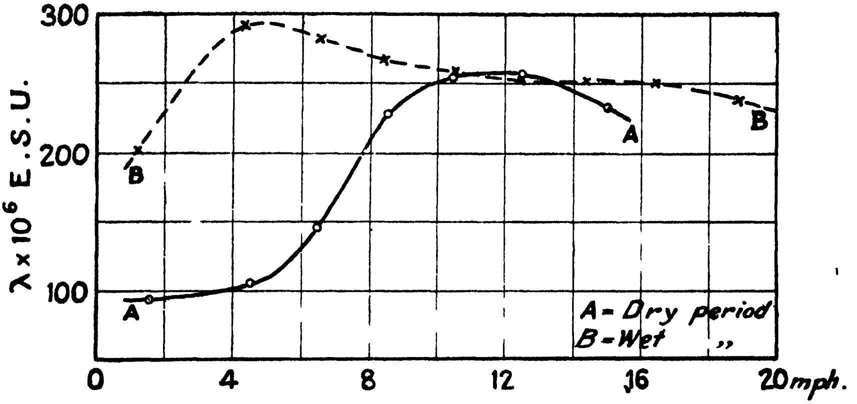


Fig. 3. Variation of Electrical Conductivity of Air at Colaba with Wind Speed

It will be seen from Figure 3 that in the dry months the conductivity shows little change up to a wind speed of about 5 m.p.h., but increases rapidly at higher speeds, the conductivity for 9 to 13 m.p.h. being nearly 1.8 times the value for winds of 3 to 5 m.p.h. Above 13 m.p.h., there appears to be a slight fall, but the number of observations rapidly decreases. In the monsoon months, the conductivity is generally greater and the variation with wind speed much less than in the dry season. The maximum conductivity is observed with winds of about 5 m.p.h.

It is not possible to extend curve A further, as at higher speeds dust is raised in the air and this influences the conductivity in a complex manner. The effect of dust-raising winds on the earth's electric field at Colaba has been discussed elsewhere[2].

The dependence of conductivity on wind speed is related to the presence of solid or liquid particles in the air, primarily smoke and dust in the dry months and sea-spray in the wet months. In the dry season, the higher wind speeds are generally associated with sea-breeze, which brings in purer air, and apparently the maximum purity of the air is reached near about 10 to 13 m.p.h. It would therefore be advisable to take routine daily observations of conductivity near about the time when this wind speed prevails, which happens generally in the afternoon. At still higher speeds, conditions change, probably due to the presence of some sea-spray in the air. During the wet period the concentration of water particles and salt nuclei near the surface which prevails during weak winds is cleared up or diluted during stronger winds and at about 5 m.p.h. the atmosphere attains the maximum purity. As the wind speed increases, it becomes gusty and sea spray begins to form and spreads inland. From curve B in Figure 3, a limiting stage in the concentration of pollution is reached, after the wind speed reaches the value of about 8 m.p.h. It is significant that the effect of wind speed in excess of 5 or 6 m.p.h. on the conductivity during the monsoon months June to September is considerably less than in the dry months. This indicates a correspondingly smaller concentration of pollution in the air during monsoon. The mean value of conductivity at about 10 to 13 m.p.h. is nearly the same in both the seasons.

2. *Effect of Dust.*—The values of conductivity observed on a few occasions when dust was raised in the air are set forth in the following Table. In columns 2 and 3 are given the values observed on the balloon tower and on the ground near the electrograph hut which is about 150 meters from the observation tower. These observations were all made in the dry season. It would appear that the conductivity on occasions when dust is raised is smaller near the ground than near the level of the tower, but at both places the values are larger than the average value. The value of $\lambda+/\lambda-$ when dust is raised in the air is greater near the ground than at the tower level.

TABLE III

Conductivity Measured on Occasions when Dust was Raised in the Air

On Tower	Near Ground	Average (Dry Period)
2.11(14)	1.90(8)	1.41
2.26(14)	1.63(8)	1.48
4.37	3.53	2.89
0.93	1.17	0.95

3. *Visibility and Conductivity.*—At the same hours at which the measurements of conductivity were made, eye-observations of visibility were taken of a number of landmarks at distances of 200 yards to 12.6 miles situated in different directions of the observation tower. For night visibility, a few selected street lights in the city were observed. In the present study, only day-light observations are analysed. The visibilities of landmarks in different directions were often different. For correlating with conductivity, the visibilities of landmarks situated in directions against the wind at the time of conductivity observations have been considered. The available observations of conductivity and visibility taken at 10 hours are used in the present analysis, as these are homogeneous and free from diurnal effects. These data are given in Table IV and plotted in Figure 4. As is to be expected, both positive and negative conductivities increase as the visibility improves.

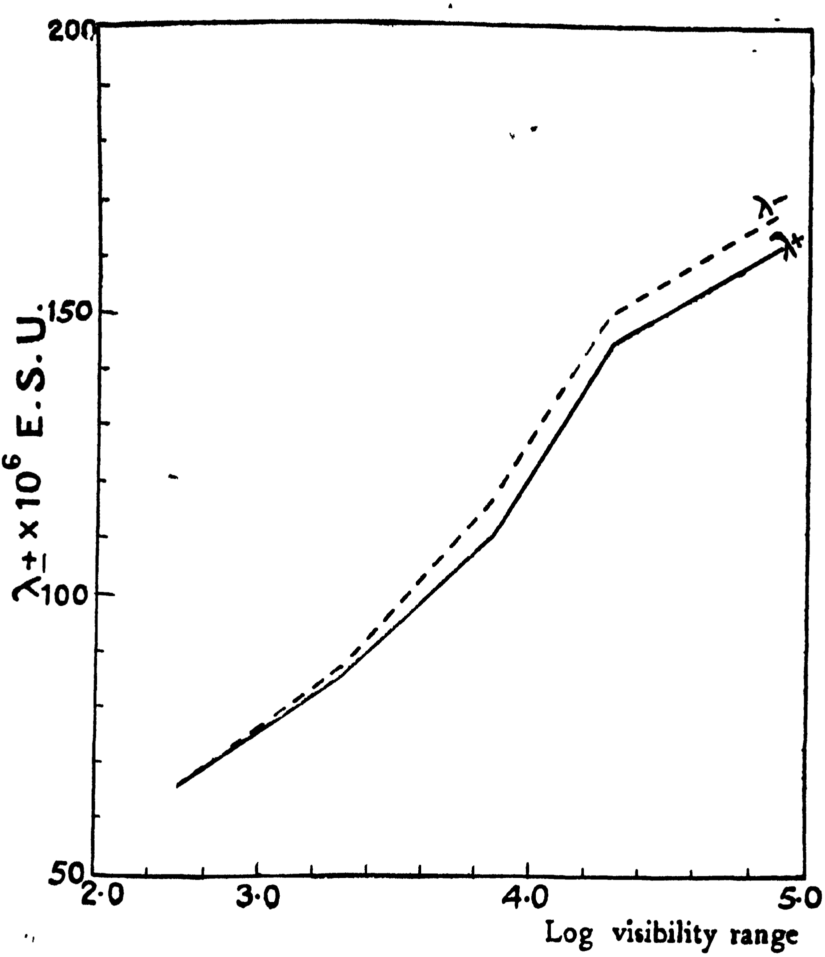


Fig. 4. Variation of Conductivity with Visibility at Colaba

TABLE IV

Variation of Conductivity with Visibility

(Unit of Conductivity = 10^{-4} E.S.U.)

Approximate Visibility Code Figures	No. of Observations	$\lambda+$	$\lambda-$	λ	q
0—3	(7)	0.66	0.66	1.32	0.98
4—5	(34)	0.86	0.87	1.73	0.99
6	(49)	1.11	1.17	2.28	0.95
7	(49)	1.45	1.50	2.95	0.97
8—9	(12)	1.62	1.68	3.30	0.96

In view of the above relationship between visibility and conductivity, it is interesting to compare the diurnal and annual variations of the two elements. The annual variations based on observations at 10 hours as well as at 6 to 18 hours are shown in Figure 5. The daylight (6 to 18 hours) observations exceed 79 in each of the months. The two series of curves are generally similar. It is however curious that while the conductivity shows a large decrease from September to October, the corresponding change in visibility takes place only in November. The diurnal variations of conductivity and visibility based on 24 hours observations on a few individual days are also found to be similar. These have been discussed elsewhere.

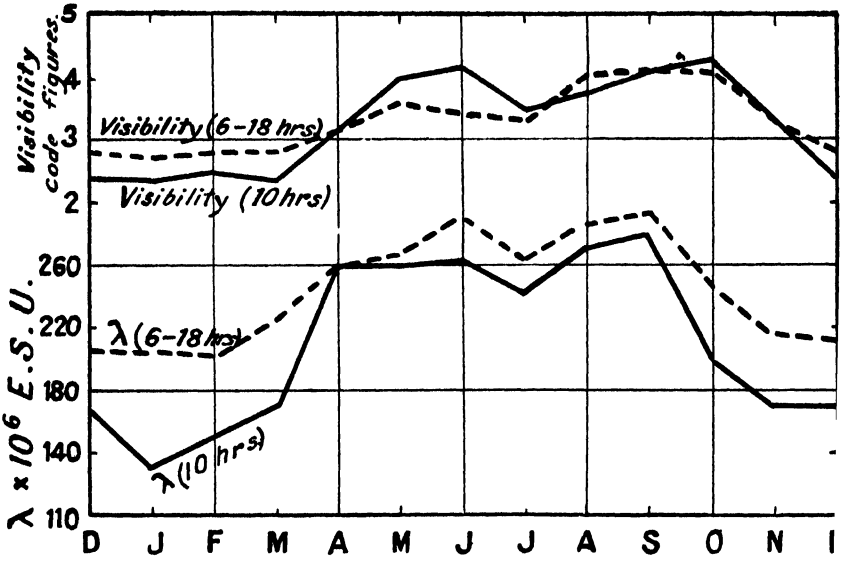


Fig. 5 Annual Variation of Visibility and Conductivity at Colaba

Diurnal and annual variations of conductivity therefore go hand in hand with visibility.

4. *Effect of Rain.*—In Table V are given the data of conductivity during, before, and after rain of different intensities. It will be seen that on the average, the positive conductivity during rain remains steady and just below the normal value. Negative conductivity on the other hand

TABLE V

Variation of Conductivity During Rain

(Unit of Conductivity $=10^{-4}$ E.S.U.)

Conductivity	Mean Value			q	Maximum		Minimum	
	$\lambda+$	$\lambda-$	λ		$\lambda+$	$\lambda-$	$\lambda+$	$\lambda-$
During light rain	1.67 (50)	1.89 (48)	3.56	0.88	2.58	4.70	0.60	0.66
During moderate rain	1.60 (15)	2.39 (16)	3.99	0.67	2.33	3.41	1.03	1.28
During heavy rain	1.70 (9)	4.37 (13)	6.07	0.39	2.85	7.79	0.98	2.87
Before light rain	2.00 (14)	2.19 (16)	4.19	0.91	3.19	3.30	1.43	1.28
Before moderate rain	1.59 (3)	1.58 (4)	3.17	1.00	1.67	1.76	1.43	1.27
After light rain	1.87 (26)	1.89 (24)	3.76	0.99	2.84	3.05	0.99	1.11
After moderate rain	2.30 (11)	2.56 (11)	4.86	0.90	2.81	3.27	1.43	1.60
Normal (wet period)	1.76	1.79	3.55	0.98	..	..	..	..

increases rapidly as the rainfall becomes heavier, being about 4 or 5% higher than normal during light rain and about 140% higher during heavy rain falls, the corresponding excesses over the positive conductivities being 10% and 160%. These features are also reflected in the values of "q", the ratio of positive to negative conductivity, which often falls to 0.1 or 0.2 in the more intense part of heavy rain.

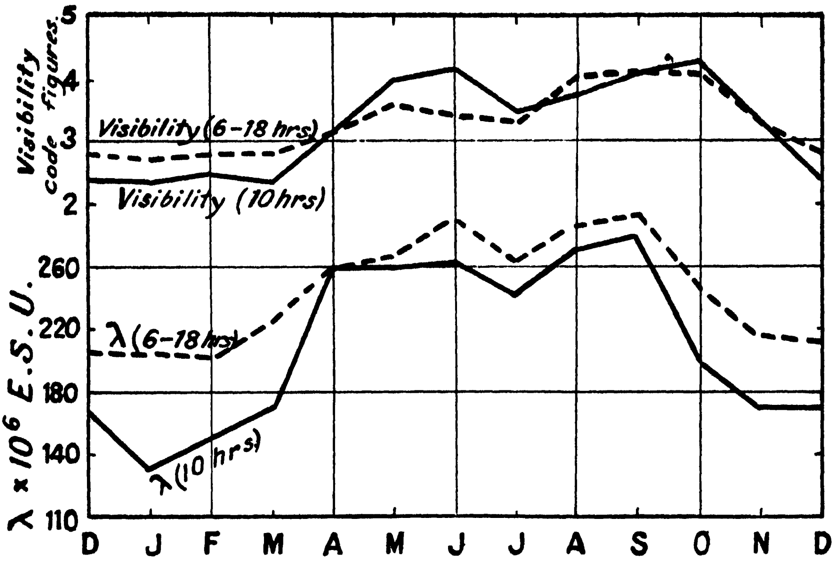
The ratios of positive to negative conductivity observed during light, heavy and very heavy rainfall at Colaba generally agree with the ratios of the number of positive to negative small ions of the air observed at Glencree 18 Km. south of Dublin during periods of rain, heavy rain and very heavy rain respectively[3].

The conductivity is greater *after* than *during* rain. This is consistent with the observations made at the Commonwealth Solar Observatory, Canberra[4].

The effect of rain on conductivity appears to be the same at the ground as on the tower.

5. A few remarks are necessary regarding the absolute values given in this note. Measurements of conductivity with the Gerdien apparatus

In view of the above relationship between visibility and conductivity, it is interesting to compare the diurnal and annual variations of the two elements. The annual variations based on observations at 10 hours as well as at 6 to 18 hours are shown in Figure 5. The daylight (6 to 18 hours) observations exceed 79 in each of the months. The two series of curves are generally similar. It is however curious that while the conductivity shows a large decrease from September to October, the corresponding change in visibility takes place only in November. The diurnal variations of conductivity and visibility based on 24 hours observations on a few individual days are also found to be similar. These have been discussed elsewhere.



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Variation of Conductivity During Rain

(Unit of Conductivity $=10^{-4}$ E.S.U.)

Conductivity	Mean Value			q	Maximum		Minimum	
	$\lambda+$	$\lambda-$	λ		$\lambda+$	$\lambda-$	$\lambda+$	$\lambda-$
During light rain	1.67 (50)	1.89 (48)	3.56	0.88	2.58	4.70	0.60	0.66
During moderate rain	1.60 (15)	2.39 (16)	3.99	0.67	2.33	3.41	1.03	1.28
During heavy rain	1.70 (9)	4.37 (13)	6.07	0.39	2.85	7.79	0.98	2.87
Before light rain	2.00 (14)	2.19 (16)	4.19	0.91	3.19	3.30	1.43	1.28
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Normal (wet period)	1.76	1.79	3.55	0.98	..	..	..	..

increases rapidly as the rainfall becomes heavier, being about 4 or 5% higher than normal during light rain and about 140% higher during heavy rain falls, the corresponding excesses over the positive conductivities being 10% and 160%. These features are also reflected in the values of "q", the ratio of positive to negative conductivity, which often falls to 0.1 or 0.2 in the more intense part of heavy rain.

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The conductivity is greater *after* than *during* rain. This is consistent with the observations made at the Commonwealth Solar Observatory, Canberra[4].

The effect of rain on conductivity appears to be the same at the ground as on the tower.

5. A few remarks are necessary regarding the absolute values given in this note. Measurements of conductivity with the Gerdien apparatus

when the wind blows straight into the instrument are found to give values about 15 to 20% greater than when the wind blows at right angles to it or obliquely. The observations discussed in this note were taken with the instrument facing east and consequently the majority of the observations correspond to an oblique direction of wind. The values of conductivity given here have therefore been corrected by a factor 120 : 100 so as to correspond to a wind direction parallel to the axis of the tube.* In the course of observations of conductivity during moderate or heavy rain the insulation occasionally broke down. This could however be rectified by removing the thin film of moisture depositing on the exposed surface of the amber insulator of the Wulf Electrometer by means of a piece of warm silk and heating the instrument. The practice of testing the insulation before and after the observations was always followed. The curves in Figure 6 exhibit the continuous variations of $\lambda+$ and $\lambda-$ for over an hour during a particular occasion of heavy rain. The corresponding rainfall and P. G. curves are also

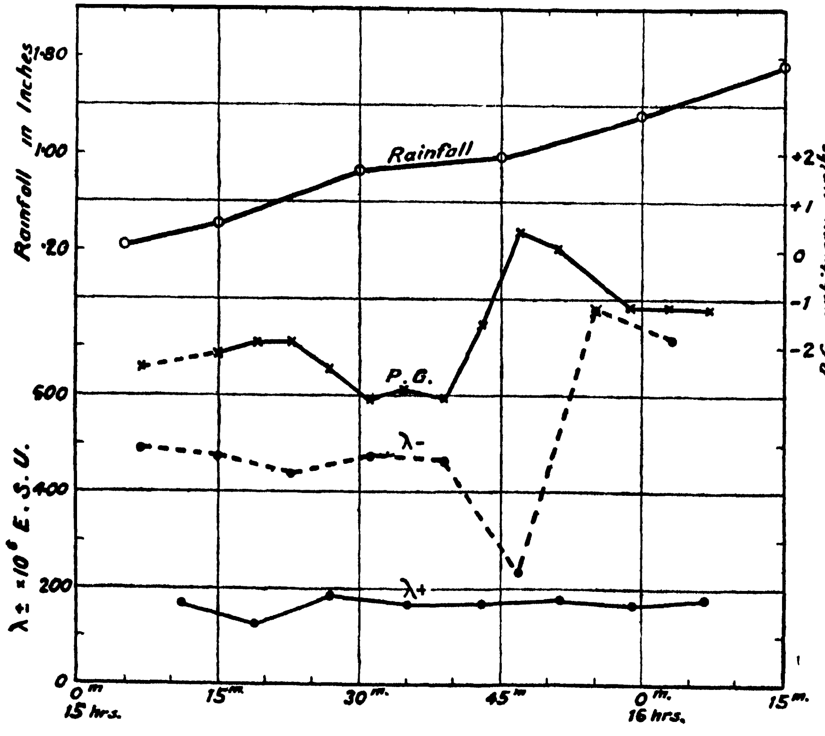

Fig. 6. Change of Conductivities during Rain : September 16, 1935

reproduced. The fomer curves show in a general way, as concluded above, how $\lambda+$ continues remarkably steady and near about the normal value. $\lambda-$ remains at a high level and occasionally shows large fluctuations. The latter roughly follows the course of the P.G., increasing as the field decreases and *vice versa*. These observations also tend to show how the insulation of the instrument continues to be satisfactory even during the period of heavy rain.

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* The necessity for this correction was pointed out to the author by Dr. Whipple in a private communication.

In Tables III and V the numbers within brackets stand for the numbers of observation.

My best thanks are due to Dr. K. R. Ramanathan for kindly criticising the paper and suggesting changes which have been incorporated in the paper.

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THE MECHANISM OF THE ACTION OF CHARCOAL ON POTASSIUM NITRATE

Part I—The Effect of Temperature, Time, etc.

By

T. M. OZA AND M. S. SHAH

SUMMARY

THE main result of the present investigation is that the equation $4KNO_3+5C \longrightarrow 2K_2CO_3+3CO_2+2N_2$ ascribed to the action of charcoal on potassium nitrate is probably made up of at least two consecutive reactions proceeding as: (I) $4KNO_3+2C \longrightarrow 4KNO_2+2CO_2$ and (II) $4KNO_2+3C \longrightarrow 2K_2CO_3+CO_2+2N_2$, of which the latter represents, in all probability, only the net result of several side or consecutive reactions.

Charcoal and potassium nitrate are two of the three ingredients (charcoal, nitre and sulphur) of gunpowder. Cumbustion of gunpowder has been much studied in the past and the reactions reported as very complicated. It is obvious that investigation of the systems (I) potassium nitrate and charcoal, (II) potassium nitrate and sulphur, and (III) potassium nitrate, charcoal and sulphur may throw considerable light on the mechanism of the reactions involved in the combustion.

The action of charcoal on potassium nitrate has been studied by Vogel (Neues Jahreb. Pharm., 1855, *4*, I) who noted that if potassium nitrate be at a temperature a little above its fusion point carbon is oxidised to carbon dioxide, and nitrogen, nitric oxide and nitrogen trioxide are formed; further, if the temperature and the proportions of the constituents are suitable a mixture of potassium nitrite and potassium carbonate is produced. Rammelsberg (Ber., 1873, *6*, 187) observed that some graphites burn in fused potassium nitrate while other varieties are not attacked. Knop (D. R. P., 93352, 1897) took a patent to prepare potassium nitrite by the reduction of potassium nitrate with charcoal. Mellor (1922, Vol. II, p. 825) states "If potassium nitrate be mixed with powdered charcoal and heated, the two materials react with explosive violence forming potassium carbonate, carbon dioxide and nitrogen: $4KNO_3+5C \longrightarrow 2K_2CO_3+3CO_2+2N_2$."

In the present work attempts have been made to study the mechanism of the interaction. Experiments have been conducted under varied conditions with weighed quantities of potassium nitrate and charcoal and, at the end of each experiment, the gaseous products of the interaction as well as the solid residue are analysed qualitatively and quantitatively.

EXPERIMENTAL

MATERIALS

Potassium nitrate.—Merck's extra pure potassium nitrate was recrystallised, dried, powdered and kept over phosphorus pentoxide for one month and used.

Charcoal.—Pure sugar charcoal was prepared according to Shah (J. C. S., 1929, 2662).

APPARATUS AND PROCEDURE

Apparatus.—The apparatus used is shown in figure 1. The column A, containing a mixture of potassium nitrate and charcoal, was connected, through the ground joint A and the tap B, to the bulb E detachable at D, and the latter was connected to the sprengel pump through the tap F. Heating was done by an electric furnace and the temperature measured by a mercury-in-silica thermometer (650°C) or a pyrometer.

Procedure.—The column AS was fitted up to the apparatus with a thin layer of warm vacuum grease and the bulb E attached, dry or half filled with a strong solution of potassium hydroxide in boiled out distilled water, as required. The apparatus was next evacuated at 100°C by a hyvac pump, followed by the sprengel pump for about 30 mts. after the first click. In most of the experiments, the tap B was kept open to the bulb E and the tap F to the sprengel pump. The furnace was adjusted to the temperature of the experiment and then brought round the column. At the end of the experiment, the electric current in the furnace was switched off and the gas pumped off. The gas was tested for carbon dioxide, carbon monoxide, oxygen, nitric oxide, nitrous oxide and nitrogen : Oxygen and nitrous oxide were found

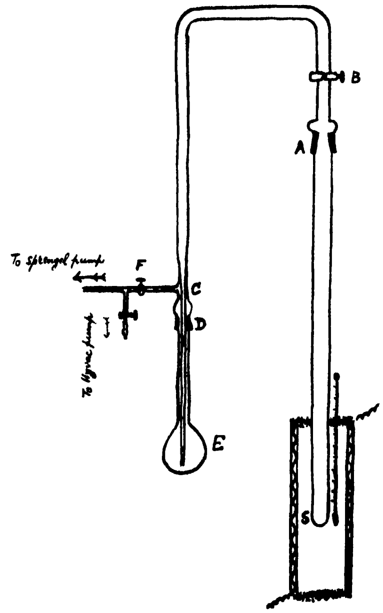

Fig. 1.

absent, carbon monoxide and nitric oxide were present in small proportions while carbon dioxide and nitrogen were the main products. After pumping off the evolved gas, the column AS was detached at A and the residue dissolved in boiled out distilled water. The solution was filtered from charcoal, diluted to 100cc and the diluted solution tested for potassium carbonate, potassium nitrite, potassium nitrate, potassium cyanide and potassium cyanate : the last two were absent. The alkali solution in the bulb E was made to 50 cc after washing the bulb and the appropriate part of the apparatus. This was examined for potassium carbonate and potassium nitrite.

ANALYSIS OF (I) GASEOUS PRODUCTS AND (II) SOLID RESIDUE

(I) *Gaseous products* :—

(*a*) The gas was measured at room temperature and pressure and analysed by absorption in standard absorbents. Carbon dioxide was first absorbed in strong KOH lye and then nitric oxide in alkaline sodium sulphite followed by strong acidified ferrous sulphate solution. Carbon monoxide was next absorbed in freshly prepared ammoniacal cuprous chloride solution followed by treatment with dilute sulphuric acid. The residual gas was taken as nitrogen. All volumes recorded are at N.T.P.

After absorption of carbon dioxide in KOH lye, the gas was tested for nitrous oxide by bubbling it through a layer of cold alcohol saturated with nitric oxide and carbon monoxide and keeping the gas over the reagent for a day : no contraction in volume indicated that nitrous oxide was absent. This treatment was dispensed with in subsequent experiments. Since some nitric oxide was always present in the gas free oxygen was taken as absent.

(*b*) Carbon dioxide and nitrogen trioxide in the bulb E were estimated as follows : for carbon dioxide, 10 cc of the solution was titrated with 0.1N HCl and then with 0.025N HCl till neutrality to phenolphthalein was obtained. Methyl orange was then added and titration continued to the end point. A blank experiment was made to see if the original KOH solution contained any carbonate but it was found to contain none. The KOH solution was always made after washing off the surface layers of the KOH sticks.

For determining the nitrogen trioxide in the alkali solution 25 or 50 cc of 0.01N $KMnO_4$ were taken in a conical flask, dilute sulphuric acid added and then a measured volume of the alkali solution poured in. The mixture was well shaken and heated to about 60°C. The excess of $KMnO_4$ was then reduced by adding a known volume of 0.01N potassium tetroxalate solution and the remaining tetroxalate titrated back with the $KMnO_4$ solution at 70°C.

The volume of carbon dioxide equivalent to potassium bicarbonate found in the titration of the bulb solution was added to that obtained in the gas analysis and the total recorded as carbon dioxide evolved in the experiment.

(II) *Solid residue* :—

(*a*) *Potassium carbonate.*—A measured volume was titrated against standard HCl using first the phenolphthalein and then methyl orange as indicator. The readings obtained were almost the same. No difficulty was experienced due to the nitrite present as quantities of the nitrite present were always small.

(*b*) *Potassium nitrite.*—This was estimated as stated in (I) *b* above.

(*c*) *Potassium nitrate.*—This was estimated by the method described in "Quantitative Chemical Analysis" by Cumming and Kay on pp. 100-01. A sodium carbonate bubbler was inserted between the carbon dioxide generator and the reaction flask.

Prior to the estimation of the nitrate, the nitrite contained in the mixture was first converted into nitrate. For this purpose, a known volume of $KMnO_4$, just a little in excess of that required for the nitrite present, was first taken in the flask, dilute sulphuric acid added and a known volume of the solution containing the nitrite and the nitrate run in from a pipette. The flask was then heated to 60°C in a water bath and connected to the apparatus.

EFFECT OF TEMPERATURE

(*a*) *Experiments with potassium nitrate and 20 per cent (on the weight of potassium nitrate) charcoal for one hour.*

Charcoal appears to interact with potassium nitrate at and above 250°C at which temperature the interaction, though extremly slow, is distinct as the residue liberates iodine from potassium iodide in presence of dilute acids though no gas is evolved.* The interaction is not appreciable upto 325°C.

An idea of the rate of the interaction was first of all obtained by conducting experiments at various temperatures. Strong KOH solution was included in the bulb E to absorb carbon dioxide (and nitrogen trioxide) evolved. The reaction, at each temperature, was arrested after one hour. At 390°C the experiment could not be continued for one hour as the reaction steadily gained speed, became violent and culminated into a flash in about 25 minutes, the whole of the column becoming deposited with a soft white deposit. The reaction then practically ceased. The result of the analysis of the reaction products are given in Table I and the relevant curves shown in Fig. 2.

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* The oxygen is probably adsorbed by charcoal and held by it in some form (Rhead, and Wheeler, J.C.S., 1913, *103*, 461 ; Keyes and Marshall, J. Amer. Chem. Soc., 1927, *49*, 158 ; Shah, *loc. cit.*).

TABLE I

Experiments with 0.375 gm. KNO_3 and 20 per cent charcoal for one hour at different temperatures.

Temp.	Gas evolved (Composition of) in c.c.s					Gas evolved (Percentage Composition of)						Residue (gms.)		
°C	Total	N_2	CO_2	NO	CO	N_2O_3	N_2	CO_2	NO	CO	N_2O_3	K_2CO_3	KNO_2	KNO_3
325	12.95	3.05	9.6	0.2	0.1	trace	23.6	74.1	1.6	0.7	..	0.019	0.012	0.3326
350	42.5	13.1	28.5	0.7	0.1	0.07	30.8	67.1	1.7	0.3	0.15	0.084	0.004	0.2515
360	49.2	16.5	31.6	0.8	0.2	0.10	33.5	64.2	1.6	0.4	0.2	0.106	0.005	0.220
370	55.5	19.3	34.6	0.9	0.5	0.22	34.8	62.3	1.7	0.9	0.4	0.119	0.013	0.181
380	100.4	39.6	58.2	1.5	0.6	0.50	39.6	58.2	1.5	0.6	0.5	0.252	0.0009	0.0035
390* Flash	74.0	28.6	41.5	1.5	1.8	0.59	38.6	56.1	2.0	2.4	0.9	0.189	0.0197	0.0753

The results show that :—(*i*) the amount of potassium nitrate used up increases with rise in temperature and along with it the amount of potassium carbonate, nitrogen and carbon dioxide, produced in the experiment, increase. Some potassium nitrate is left in the system, even after the flash, presumably due to lack of charcoal in the system (a good amount of charcoal is hurled out of the system during the flash) ; (*ii*) A comparison of the amounts of nitrogen, carbon dioxide and potassium carbonate produced in experiments upto 390°C shows that (*a*) there is a regular relation between the amounts of nitrogen and potassium carbonate formed ; (*b*) the amounts of nitrogen are lower and those of carbon dioxide higher in experiments at low temperatures than those in experiments at high temperatures ; (*iii*) in experiments upto 380°C, the amounts of nitric oxide, carbon monoxide and nitrogen trioxide are smaller than in experiments at 390°C ; (*iv*) in experiments upto 380°C, the amounts of potassium nitrite do not show any regularity.

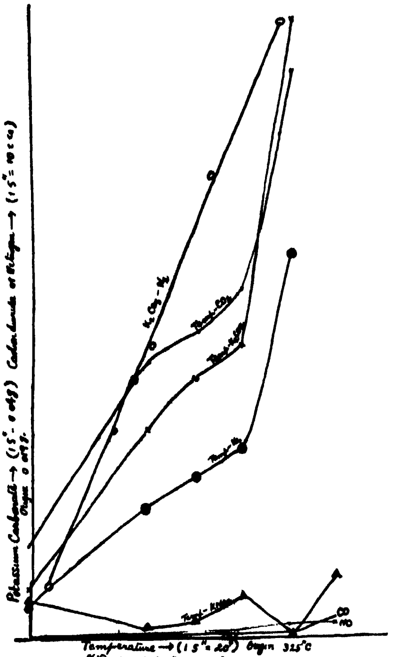

Fig. 2.

Fig. 2 shows conspicuously the rectilinear relation between nitrogen and potassium carbonate produced in the experiments.

(*b*) *Experiments with potassium nitrate and 20 per cent charcoal till the evolved gas exerted the same pressure.*

In the above experiments, the amounts of potassium nitrite in the residue do not show regularity as the other reaction products do. Thinking that some information on this point may be obtained if the reaction were arrested at practically the same stage, experiments were conducted at different temperatures with the same quantities of potassium nitrate and charcoal as before and the interaction arrested when the evolved gas exerted the same pressure (which was due mainly to nitrogen). The results of this series of experiments are given in Table II. Fig. 3 shows times and quantities of potassium nitrite plotted against temperature.

TABLE II

Experiments with 0.375 gm. KNO_3 and 20 per cent charcoal at different temperatures till the evolved gas exerted the same pressure.

Time required	Temp.		Gas evolved (Composition of)					Gas evolved (Percentage Composition of)					Residue (gms.)		
Mts.	°C	Total	N_2	CO_2	NO	CO	N_2O_3	N_2	CO_2	NO	CO	N_2O_3	K_2CO_3	KNO_2	KNO_3
1800	315*	67.7	23.7	43.2	0.5	0.0	0.3	35.0	63.8	0.7	0.0	0.4	0.155	0.0035	0.1578
540	330	63.4	22.3	40.0	0.4	0.4	0.3	35.2	63.1	0.6	0.6	0.4	0.142	0.0059	0.1684
150	350	62.5	23.5	37.5	0.2	1.2	0.08	37.6	60.0	0.3	2.0	0.1	0.149	0.0046	0.1610
65	370	60.8	23.0	37.0	0.1	0.5	0.24	37.7	60.8	0.2	0.8	0.4	0.149	0.0067	0.1630
25	380	60.2	23.0	36.1	0.3	0.7	0.18	37.8	60.0	0.5	1.2	0.3	0.150	0.0070	0.1625

*The first experiment in this series was carried out at 315°C instead of at 325°C (preceding series) with a view to obtain, if possible, a larger amount of KNO_2 in the residue and a high percentage of CO_2 in the gaseous products.

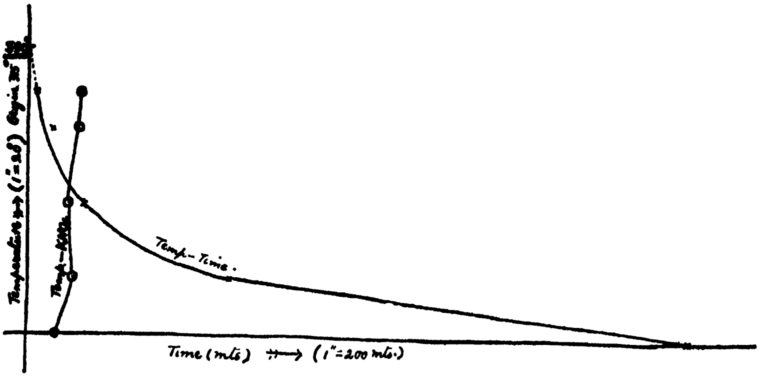

Fig. 3.

The results show that (*i*) potassium nitrite is always produced in the interaction and its amounts vary irregularly with temperature; (*ii*) the amount of nitrogen trioxide produced in 30 hrs. at 315°C is much greater than that produced in 1 hr. at 325°C.

EFFECT OF PRESSURE OF EVOLVED GAS AND OF MASS OF POTASSIUM NITRATE

(*c*) *Experiments with different amounts of potassium nitrate and 20 percent charcoal allowed to proceed to different stages.*

The experimental results given in Tables I and II show that the amounts of nitrogen and potassium carbonate produced depend upon the extent to which the interaction proceeds and is independent of temperature, whereas the proportion of carbon dioxide and potassium nitrite depend both on the temperature of the experiment and the extent to which the experiment is allowed to proceed. With a view to see how far the production of carbon dioxide and of potassium nitrite depends upon the extent of the interaction, experiments were undertaken with the same quantities of potassium nitrate and charcoal as in the preceding series, at 375°C—a temperature at which the interaction proceeds with a fairly moderate speed—and checked when the pressure of the evolved gas (mainly nitrogen) was 10, 20, .. etc. cms. of mercury (*a*). As 0.375 g. potassium nitrate, used in the experiments, could not produce gas sufficient to exert pressure greater than 30 cms. of mercury these experiments were repeated with (*b*) 0.889 g.potassium nitrate and the usual proportion of charcoal, the experiments in this latter case being checked when the pressure of the evolved gas was 3, 6, 10, ... etc. cms. of mercury. Incidentally a comparison of the results of the two series of experiments showed the effect of mass on the interaction. The results of this series of experiments are given in Table III(a) and (b) and the graphs of time, nitrogen, potassium carbonate and potassium nitrite against pressure and of nitrogen against potassium carbonate shown in Fig. 4.

TABLE III

Experiments with (a) 0.375 gms. and (b) 0.889 gms. KNO_3 and 20 per cent charcoal at 375°C till the pressure of the evolved gas was 10,20,30 cms. of Hg. in (a) and 3, 6, 10, 20, ..., 70 cms. of Hg. in (b)

(*a*) :—

Press. cms. (Hg)	Time (mts.)	KNO3 taken (gm.)	Gas evolved (Composition of) in c.cs.						Gas evolved (Percentage Composition of)				Residue (gms.)		
			Total	N_2	CO_2	NO	CO	N_2O_3	N_2	CO_2	NO	CO	N_2O_3	K_2CO_3	KNO_2	KNO_3
10	22	0.3792	34.1	9.6	23.5	0.8	0.2	0.26	28.1	68.9	2.4	0.6	0.8	0.062	0.0054	0.2820
20	41	0.3785	60.8	22.0	37.9	0.3	0.6	0.13	36.1	62.2	0.5	1.2	0.2	0.149	0.0067	0.1730
30	63	0.3764	81.3	32.0	47.8	1.1	0.4	0.08	39.3	58.8	1.3	0.6	0.09	0.196	0.0040	0.0816
(*b*) :—																
3	7	0.8900	15.8	4.1	11.3	0.3	0.1	0.08	25.9	71.5	1.9	0.6	0.5	0.028	0.0358	0.8097
6	—	0.8930	27.3	7.3	19.5	0.4	0.1	—	26.7	71.0	1.4	0.3	—	—	—	—
10	18	0.8897	38.0	10.9	26.3	0.5	0.3	0.12	28.7	69.4	1.2	0.8	0.3	0.066	0.0260	0.7592
20	33	0.8880	61.1	21.4	38.6	0.5	0.6	0.04	35.1	63.3	0.7	1.0	0.07	0.136	0.0231	0.6701
30	45	0.8908	87.8	34.0	53.8	0.5	0.7	0.08	38.2	60.4	0.6	0.8	0.09	0.2005	0.0314	0.5518
40	56	0.8932	120.8	44.7	75.0	0.5	0.6	0.09	37.0	62.1	0.4	0.5	0.08	0.2620	0.0358	0.4553
60	88	0.8740	173.0	69.1	102.3	1.0	0.6	0.07	40.0	59.1	0.5	0.4	—	0.4070	0.0363	0.2177
70	113	0.8945	200.0	82.4	116.1	1.0	0.6	0.08	41.2	58.0	0.5	0.3	0.04	0.4810	0.0120	0.1500

Note :—1. The mass of K_2CO_3 produced per 1 c.c. N_2 is about 0.006 gm.

2. The ratio N_2:CO_2 is about 1:2.7 at the commencement; it slowly diminishes from top to bottom and becomes 1:1.4 at end.

3. The ratio N_2:CO_2, appertaining to the amounts of these between consecutive stages, are: 1:2.7; 1:2.5; 1:1.9; 1:1.2; 1:1.2 1:1.2; 1:1.1; and 1:0.96, respectively from top to bottom in Table III (*b*).

The results confirm all the observations previously made and further show that: (*i*) at low pressures, *i.e.*, at the commencement of the reaction, the amount of carbon dioxide is higher and of nitrogen smaller than that at high pressures, *i.e.*, as the experiment proceeds; (*ii*) the amount of nitrogen formed in the last stage, wherein the quantity of potassium nitrite in the residue is much less than in the preceding stage. is greater even than that of carbon dioxide and this in spite of the fact that some potassium nitrate is used up in the stage which must have introduced some carbon dioxide.

Again, when the results of experiments in (*a*) are compared with those in (*b*), it is clear that the effect of mass of potassium nitrate on (*i*) the speed of the reaction and (*ii*) the production of carbon dioxide and nitrogen is very small, but its effect on (*iii*) the amounts of potassium nitrite in the residue is very marked: the amount of potassium nitrite produced is greater the greater the mass of potassium nitrate used in the experiment.

Fig. 4 shows that the nature of proportionality between potassium carbonate and nitrogen in these experiments is exact and that each of these is linearly proportional to pressure.

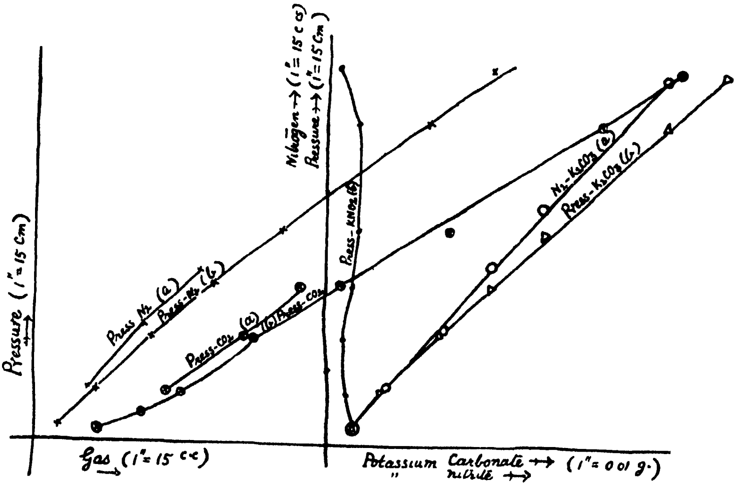

Fig. 4.

(*d*) *Effect of removal of the evolved gas on the interaction.*

From the results of all the experiments given above, it is clear that the proportions of potassium carbonate and nitrogen produced in the interaction are throughout regular whereas those of potassium nitrite and carbon dioxide are higher (*i*) at low temperatures and when the interaction is arrested after a short time and when the interaction is allowed to proceed for a long time (Expt. I, Tables I and II) and (*ii*) at the commencement of the interaction than in subsequent stages (*vide* Table II). Thus it appears highly probable that during the interaction potassium nitrite is used up as it is formed, with the result that the amounts of carbon dioxide, nitrogen and potassium carbonate are affected. With a view to test the formation of potassium nitrite and its subsequent effect on the relative production of carbon dioxide, nitrogen and potassium carbonate, experiments were conducted in which (*i*) carbon dioxide (and nitrogen oxides absorbable by KOH) and (*ii*) all the evolved gas, *i.e.*, nitrogen, and other gases also, was removed as it was formed. The temperature chosen for the experimentation was 390°C as it was expected that the effect of the removal of (*i*) and (*ii*) would be conspicuous if the rate of production of potassium nitrite is great. Two sets of experiments were performed at 390°C extending over different periods of time : in the first set the KOH solution in the bulb E was not used and the evolved gas was all pumped off continuously during the progress of the experiment while in the second set KOH solution was used to absorb carbon dioxide (and of course, absorbable nitrogen oxides, as usual) and nitrogen with unabsorbed gaseous products allowed to accumulate in the system. The results of analysis of the gaseous products and the solid residue in these two sets of experiments are given in Table IV. Fig. 5 shows the type of graphs obtained by plotting potassium nitrite, potassium carbonate, nitrogen, carbon dioxide, and potassium nitrate used up against time and nitrogen against potassium carbonate, in either set of experiments.

These results show that : (*i*) the interaction proceeds more rapidly when carbon dioxide is removed than when carbon dioxide and nitrogen both are pumped off. In the former case the reaction becomes violent and ultimately results into a flash, whereas in the latter case the interaction proceeds smoothly upto a particular extent and then becomes slow, presumably because one of the reactants is used up or its amount has become very low ; (*ii*) the amounts of potassium nitrite in the residue are greater in experiments where carbon dioxide is removed than in experiments where both carbon dioxide and nitrogen are pumped off, inspite of the fact that the larger mass of potassium nitrate used in the latter set has the effect of increasing the production of potassium nitrite (mass effect, Table III). This shows that the presence of nitrogen increases the stability of potassium nitrite ; (*iii*) the amounts of nitrogen are greater and those of carbon dioxide are smaller in experiments where carbon dioxide is removed than in experiments where all the evolved gas is pumped off ; (*iv*) in both sets of experiments, oxides of nitrogen are evolved but the amounts appeared to be greater in experiments where all the evolved gas is pumped off than in experiments where car-

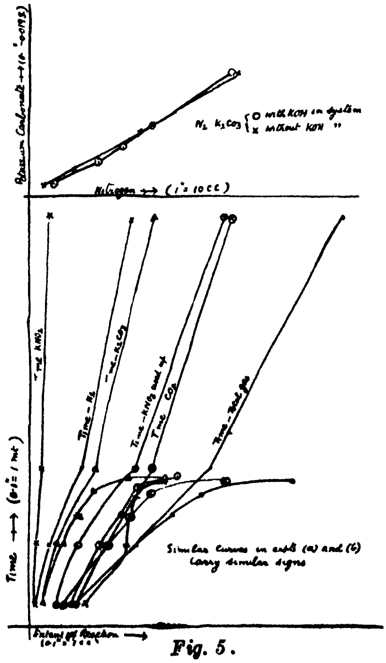

Fig. 5.

TABLE IV*

Experiments with KNO_3 and 20 per cent charcoal at 390°C to examine the interaction in stages.

(*a*) Without using KOH :—

1	2	3						4		5	6					7		
Duration of stage	KNO_3 taken	Gas evolved (Composition of) in c.cs.						Diff. between consecutive stages		Ratio N_2: CO_2	Gas evolved (Percentage Composa'ion of)					Residue (gms.)		
T(mts.)	(Gms.)	Total	N_2	CO_2	NO	CO	N_2O_3	N_2	CO_2	from 4	N_2	CO_2	NO	CO	N_2O_3	K_2CO_3	KNO_2	KNO_3
4	0.5001	19.3	2.2	15.8	0.7	0.6		2.2	15.8	1:7.2	11.8	81.9	3.7	3.1		0.0136	0.0009	0.4571
14	0.4990	36.0	7.0	27.3	0.9	0.8		4.8	11.5	1:2.4	26.4	69.3	2.5	2.2		0.0435	0.0009	0.4172
27	0.5010	61.8	18.5	41.8	0.8	0.7		11.5	14.5	1:1.3	30.0	67.8	1.3	1.1		0.1068	0.0022	0.3186
70	0.5000	108.5	36.3	69.5	1.1	1.6		17.8	27.5	1:1.5	33.4	64.5	1.0	1.5		0.2130	0.0035	0.1608
(*b*) Using	KOH:—																	
4	0.4000	21.1	3.9	15.9	0.8	0.5	0.13	3.9	15.9	1:4.1	18.6	75.7	4.0	2.4	0.6	0.0200	0.0103	0.3404
14	0.4000	36.7	11.5	23.7	1.1	0.4	0.15	7.8	7.6	1:1	31.3	64.5	3.0	1.1	0.4	0.0540	0.0169	0.2688
19	0.3985	49.1	15.8	31.9	0.8	0.6	0.14	4.3	8.2	1:1.9	32.3	64.8	1.8	1.2	0.3	0.0940	0.0169	0.2342
23	0.3985	59.1	20.6	36.9	1.0	0.6	0.17	10.0	4.8	1:0.5	34.2	63.1	1.8	1.0	0.3	0.1230	0.0183	0.1895
25* Flash	0.4000	91.4	34.4	52.2	1.8	3.0	0.51	13.8	15.3	1:1.1	37.6	57.1	2.0	3.3	0.6	0.2160	0.0233	0.0562

*The amount of KNO_2 in the residue is greater in (*b*) than in (*a*) inspite of the fact that larger mass of KNO_3 is used in (*a*) than in (*b*). The effect of increase in mass of KNO_3 with otherwise identical conditions, is to produce larger amounts of KNO_2 (*vide* Table III).

bon dioxide alone is removed. In the former experiments, mercury of the pump was affected and the effect was greater particularly at the commencement of the interaction.

Fig. 5 shows that there is a sudden change in the gradient of curves corresponding to experiments where carbon dioxide alone is removed by the KOH solution. This indicates that the interaction follows a different course after a particular time. The absence of such a change in the curves corresponding to the other set of experiments where the evolved gas is all pumped off appears to account for the absence of a flash in these experiments.

INTERPRETATION OF RESULTS

The bearing of all these observations on the interaction between potassium nitrate and charcoal is that charcoal tends to interact with potassium nitrate at about 250°C—a temperature much below the melting point of potassium nitrate. The high production of carbon dioxide and potassium nitrite in the initial stages of the interaction shows that charcoal induces the reduction of potassium nitrate to potassium nitrite with the production of carbon dioxide as

$$4KNO_3+2C\longrightarrow 4KNO_2+2CO_2 \ldots\ldots\ldots\ldots\ldots (1).$$

Since at all stages of the interaction nitrogen and potassium carbonate are always present and that too in regular increasing proportions with the progress of the interaction, and since potassium nitrite never accumulates, on the other hand, it is found to be present in very small proportions, *i.e.*, in amounts much below the expected values according to (I), it seems probable that charcoal tends to interact with potassium nitrite immediately it is produced in (I) leading to the formation of potassium carbonate and nitrogen as the main products. The facts that with the rise in temperature (*i*) the proportions of carbon dioxide produced diminish, and (*ii*) those of potassium carbonate and nitrogen increase in linear proportions, show also that potassium nitrite interacts with charcoal as soon as it is formed. Further (*i*) the violent interaction occurs under conditions favourable for the accumulation of potassium nitrite in the residue, *i.e.*, when carbon dioxide and not both the carbon dioxide and nitrogen are pumped off, (*ii*) the amounts of potassium nitrite left in the residue after the violent interaction are greater than under other conditions, also conform to the same view. This fact when taken in conjunction with the observation that the amount of nitrogen, in stages wherein potassium nitrite is used up, is greater even than that of carbon dioxide, and this too inspite of the fact that some potassium nitrate is used up during the process which must have introduced some carbon dioxide, shows that potassium nitrite interacts with charcoal so as to produce a comparatively large quantity of nitrogen in some such way as

$$4KNO_2+3C\longrightarrow 2K_2CO_3+CO_2+2N_2 \ldots\ldots\ldots\ldots\ldots (2).$$

The formation of nitric oxide, nitrogen trioxide and carbon monoxide, which has always been observed, could be accounted for only after the violent interaction observed and the role of potassium nitrite in the interaction are more closely studied. This has been done and the results will soon be communicated.

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THE M. R. SCIENCE INSTITUTE,
GUJARAT COLLEGE, AHMEDABAD

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THE THERMAL DECOMPOSITION OF POTASSIUM NITRITE

By

T. M. Oza and M. S. Shah

Summary

TWO important observations have been made : (1) Nitrogen tetroxide is produced at the commencement of the decomposition ; (2) nitrogen is produced in proportions greater than required by the equation : $4KNO_2 \longrightarrow K_2O+2KNO_3+NO+N$ (Ray : J.C.S., 1905, T., 87, 177).

The experimental results, on the whole, tend to show that the primary stage in the thermal decomposition of potassium nitrite is $2KNO_2 \rightrightarrows K_2O+NO+NO_2$ (1). The nitrogen tetroxide produced reacts with the undecomposed potassium nitrite to produce nitrogen and nitric oxide according to : $4KNO_2+2NO_2 \longrightarrow 4KNO_3+N_2$ (2) and $KNO_2+NO_2 \longrightarrow KNO_3+NO$ (3) in agreement with the suggestion of Oswald (Ann. Chim., 1914, (IX), *1*, 32-112). The potassium nitrate, thus produced, decomposes under the experimental conditions as $2KNO_3 \longrightarrow 2KNO_2+O_2$ and the oxygen produced, together with the nitric oxide present in the system, affects the reactions (1), (2) and (3).

The thermal decomposition of alkali and alkaline earth nitrites has been studied in the past. Ray (*loc. cit.*) studied the thermal decomposition of sodium, calcium, barium and magnesium nitrites by heating small quantities of these under vacuum in two stages : in the first where the heating was slow and cautious he obtained a mixture of nitric oxide and nitrogen (with nitrous anhydride in traces) and in the second where the heating was much more intense he obtained a reddish brown gas and oxygen. He therefore concluded that in the first stage nitric oxide is the main gaseous product of the decomposition and that a portion of the salt is converted into nitrate, while in the second stage it is the nitrate which undergoes decomposition giving off oxygen. He represented the two stages by means of the equations :

Initial : $3Ba(NO_2)_2 \longrightarrow 2BaO + Ba(NO_3)_2 + 4NO$ . . . . (*i*)

$2Ba(NO_2)_2 \longrightarrow BaO + Ba(NO_3)_2 + NO + N$ . . . (*ii*)

Final : $Ba(NO_3)_2 \longrightarrow BaO + 2NO_2 + O$ . . . . (*iii*)

whilst intermediate between these there is also

$Ba(NO_3)_2 \longrightarrow Ba(NO_2)_2 + O_2$ . . . . (*iv*)

In his opinion, several reactions go on side by side some of which, probably, overlap so that no sharp line of demarcation can be laid down between them.

Oswald (*loc. cit.*) studied the decomposition of alkali nitrites and found that potassium nitrite begins to decompose at 350°C according to the following equations :

$3KNO_2 \longrightarrow K_2O + KNO_3 + 2NO$ . . . . (*i*)

$5KNO_2 \longrightarrow K_2O + 3KNO_3 + 2N$ . . . . (*ii*)

He studied, also, the action of nitric oxide and nitrogen tetroxide upon the dry nitrites and found that the dry salt was not acted upon by nitric oxide so long as the decomposition itself did not occur and that nitrogen tetroxide oxidised potassium nitrite to potassium nitrate. He suggested two more reactions represented by the following equations :

$NaNO_2 + NO_2 \longrightarrow NaNO_3 + NO$ . . . . (*iii*) and

$2NaNO_2 + NO_2 \longrightarrow 2NaNO_3 + N$ . . . . (*iv*)

Butkov and Chassovenni (Acta. Physicochim, U.R.S.S., 1936, *5*, 137-159) studied the thermal dissociation and absorption spectra of vapours of potassium nitrite and potassium nitrate amongst others and found that on heating these in an evacuated quartz tube and examining the products spectrographically in the range 7000-1880 A, potassium nitrate gave nitric oxide at temperatures>550°C and nitrogen tetroxide on cooling; potassium nitrite behaved similarly except that on cooling nitric oxide persisted and no nitrogen tetroxide was formed.

Quantitative experiments on the thermal decomposition of potassium nitrite were undertaken to investigate the effect of (*i*) time at a constant temperature, (*ii*) temperature at constant time and (*iii*) mass at a constant temperature, on the relative production of the reaction products. The results of these experiments are set out in this paper.

EXPERIMENTAL

Potassium nitrite required in this work was prepared by recrystallisation from the Merck's pure potassium nitrite. It gave on analysis the following results:

(*i*) 1.3717 g. substance gave, on treatment with conc. sulphuric acid, 1.4215 g. K_2SO_4. (Theoretical value : 1.4039 g.).

(*ii*) 0.2226 g. substance required 53.6 cc. 0.0984 N $KMnO_4$ soln. (Theoretical value : 53.2 cc.).

Found : K=46.4 per cent, NO_2=54.1 per cent; calcd. for KNO_2: K=45.9 per cent, NO_2 =54.2 per cent.

APPARATUS AND PROCEDURE

These were the same as those described under 'The Mechanism of the Action of Charcoal on Potassium Nitrate, Part I' by the authors (this issue, p. 57). The substance was heated electrically in a vacuum at the bottom of a 2-ft. vertical column the ground glass top of which was connected to the sprengel pump through an internal seal which allowed the gaseous products to reach the pump only after bubbling through a strong KOH solution. Potassium nitrite began to decompose at its melting point (about 419°C) and the decomposition was very slow upto 515°C. A blue litmus paper kept near the top of the vertical column became reddened as soon as the decomposition started. The evolved gas was examined for nitric oxide and nitrogen, nitrous anhydride (*giving nitrogen tetroxide*) being obtained by analysis of the KOH solution and the residue for potassium oxide, potassium nitrite and potassium nitrate. The methods employed were the same as those stated in the above paper except that potassium oxide* was determined by direct titration against standard succinic acid. The results of experiments on the effect of time, temperature and mass are given in Tables, I, II and III respectively.

The results show that

(*i*) some nitrogen tetroxide is produced (as also potassium nitrate) and its amount, though very small, increases with the period of heating ; (*ii*) nitric oxide and nitrogen, the main gaseous products, increase with the period of heating. The proportion of nitric oxide, which is considerable at the start, goes on diminishing while that of nitrogen, which is small at the start, goes on increasing with increase in the period of heating. This indicates that with progressive heating reactions come into being which probably consume nitric oxide and produce nitrogen ; (*iii*) the amounts of potassium nitrite used up and those of potassium oxide and potassium nitrate formed go on increasing with the increased period of heating, the rate of formation of potassium oxide being greater than that of potassium nitrate ; (*iv*) the amounts of potassium nitrite used up and potassium nitrate formed per cc of the evolved gas diminish whereas those of potassium oxide formed increase steadily as heating is prolonged.

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* As glass was invariably corroded, the results of K_2O determination are not absolute ; they serve, however, the purpose of comparison.

TABLE I

Experiments on decomposition of potassium nitrite at 515°C for different periods of time.

Period of heating	KNO_2 used	Total evolved gas	Evolved gas per cent			Residue (gms.)			KNO_2 used up	Per c.c. evolved gas		
T (hrs.)	gms	c.cs. at N.T.P.	NO.	N_2	N_2O_3	K_2O	KNO_2	KNO_3		KNO_2 used up	KNO_2 used up	KNO_3 formed.
8	0.2950	4.1	73.2	21.9	5.0	0.0056	0.2523	0.0217	0.0427	0.0014	0.0104	0.0053
16	0.3127	7.1	62.0	34.5	4.2	0.0130	0.2391	0.0392	0.0736	0.0018	0.0103	0.0055
64	0.2905	19.8	43.0	51.8	5.5	0.0400	0.1342	0.0763	0.1563	0.0020	0.0079	0.0038
72	0.2950	21.2	42.4	52.3	5.7	0.0452	0.1112	0.0834	0.1838	0.0021	0.0087	0.0039

TABLE II

Experiments on decomposition of potassium nitrite at different temperatures for 17 hours.

KNO_2 used	Temp.	Total evolved gas	Evolved gas per cent			Residue (gms.)			KNO_2 used up	Per c.c. evolved gas		
gms	°C	c.cs at N.T P.	No	N_2	N_2O_3	K_2O	KNO_2	KNO_3		K_2O formed	KNO_2 used up	KNO_3 formed
0.5952	440	5 9	64.4	32.2	3.5	0 0221	0.5120	0.0349	0.0872	0.0037	0.0148	.0059
0.5990	500	10.0	46 0	51 0	3 0	0 0228	0.4293	0.1028	0.1697	0.0023	0.0170	0.0103
0.5982	540*	19.4	30 0	69 0	1 0	0 0357	0.3145	0.1651	0.2873	0.0018	0.0146	0.0085

* The heating Column had got flattened by softening in this experiment

The results show that

(*i*) some nitrogen tetroxide is evolved and its amount, though small, is greater at 500°C even than at 540°C ; (*ii*) just as in Table I nitric oxide and nitrogen are the main gaseous products and their proportions differ at different temperatures, nitrogen increasing and nitric oxide diminishing with increase in temperature ; (*iii*) the amounts of potassium nitrite used up and those of potassium oxide and potassium nitrate formed increase with the increase in temperature. The rate of increase of potassium oxide is very small upto 500°C and fairly great beyond it while that of potassium nitrate is large and fairly uniform ; (*iv*)amounts of potassium oxide formed per cc of the evolved gas diminish regularly with rising temperature, while those of potassium nitrite used up and potassium nitrate formed increase upto 500°C and diminish at 540°C.

The results show that

(*i*) some nitrogen tetroxide is evolved and its amount diminishes with an increase in the mass of potassium nitrite used ; (*ii*) nitric oxide and nitrogen are, as usual, the main gaseous products and their proportions are considerably affected by the mass of potassium nitrite used in the experiment, nitrogen showing a sudden increase and nitric oxide showing a sudden decrease, with the increase in the mass of potassium nitrite used; (*iii*) the amounts of potassium nitrite used up and those of potassium oxide and potassium nitrate formed increase with the mass of potassium nitrite used.

Discussion of Results

The never-failing presence of nitrogen tetroxide and nitric oxide in the gaseous products of the reaction together with the fact that nitric oxide is produced in large quantity in the initial period of heating under all conditions of experiment show that nitric oxide and nitrogen tetroxide may be the primary products of the decomposition of potassium nitrite which proceeds, in all probability as,

$$2KNO_2 \rightleftharpoons K_2O + NO + NO_2 \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The amounts of nitrogen tetroxide actually found are much less than those of nitric oxide, which may be due (see Oswald, *l c. ci* .) to a rapid reaction between it and potassium nitrite resulting in the formation of nitrogen or nitric oxide or both according to :

$$4KNO_2 + 2NO_2 \longrightarrow 4KNO_3 + N_2 \ldots\ldots\ldots\ldots (2)$$

$$KNO_2 + NO_2 \longrightarrow KNO_3 + NO \ldots\ldots\ldots\ldots (3)$$

The occurrence of distinct, though small, variations in the proportion of nitrogen tetroxide in different experiments shows that this gas takes part in the reaction. That its amounts become small at elevated temperatures (Table II) and with the use of larger masses of potassium nitrite used (Table III) shows that it is used up more effectively under these conditions. It will be seen also that these are just the conditions under which potassium nitrate is more effectively produced. This means that

TABLE III

Experiments on decomposition of potassium nitrite with varying mass at 500°C for 17 hours.

KNO_2 used	Total evolved gas	Evolved gas per cent			Residue (gms.)			KNO_2 used up		Per c.c. evolved gas	
gms.	c cs at N.T.P.	NO	N_2	N_2O_3	K_2O	KNO_2	KNO_3		K_2O formed	KNO_2 used up	KNO_3 formed
0.3000	7.5	74.7	18.4	6.5	0.0132	0.2167	0 0422	0.0833	0.0017	0.0111	0.0056
0.5990	10.0	46.0	51.0	3.0	0.0288	0.4293	0.1028	0.1697	0.0029	0.0170	0.0103
0.9005	11.3	29.2	68.1	2.7	0.0415	0.6400	0.1480	0.2605	0.0037	0.0230	0.0131
1.1960	12.1	15.7	81.8	2.5	0.0545	0.9053	0.1804	0.2907	0.0045	0.0240	0.0149

the conditions under which nitrogen tetroxide is used up are precisely those under which potassium nitrate is more effectively produced as demanded by equation (2). The amounts of nitrogen go on increasing and those of nitric oxide go on diminishing under the conditions of all these experiments indicating that with the progress of the decomposition reactions come into being which consume nitric oxide and produce nitrogen. The amounts of potassium nitrate also increase under all these conditions. In view of the fact that this substance undergoes decomposition under the conditions of these experiments producing potassium nitrite and oxygen (Ray, *loc. cit*). or nitric oxide and oxygen (Butkov and Chassovenni, *loc. cit.*), the consumption of nitric oxide and formation of nitrogen become intelligible through the intermediate formation of nitrogen tetroxide from oxygen of the potassium nitrate, the nitrogen tetroxide reacting as in (2). Nitric oxide may be removed from the system also by the reaction $K_2O+NO+NO_2 \longrightarrow 2KNO_2$ set in as a result of lack of balance in the relative concentrations of the reaction products induced by the decomposition of potassium nitrate. The reaction (*1*) is therefore reversible.

CONCLUSION

All observations made above indicate that the fundamental reaction in the decomposition of potassium nitrite is

$$4KNO_2 \rightleftharpoons 2K_2O+2NO+2NO_2 \ldots\ldots\ldots\ldots (1)$$

$$\uparrow\downarrow$$

$$(2\ NO+O_2)$$

A part of the nitrogen tetroxide escapes and its presence is noted and the remainder simultaneously interacts with the undecomposed potassium nitrite forming (*i*) potassium nitrate and nitrogen and (*ii*) potassium nitrate and nitric oxide, as suggested by Oswald, as :

$$4KNO_2+2NO_2 \longrightarrow 4KNO_3+N_2 \quad \ldots\ldots\ldots\ldots (2)$$

$$KNO_2+NO_2 \longrightarrow KNO_3+NO \quad \ldots\ldots\ldots\ldots (3)$$

The potassium nitrate produced in (2) and (3) undergoes decomposition side by side as $2KNO_3 2KNO_2 + \longrightarrow O_2$, the tendency of this re action being great because of the presence of nitric oxide in the system which removes the oxygen formed as $2NO+O_2=2NO_2$, the tetroxide produced affecting all the reactions (1), (2) and (3).

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GUJARAT COLLEGE, AHMEDABAD,
AND
KARNATAK COLLEGE, DHARWAR

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MUTUAL COAGULATION OF COLLOIDAL SOLUTIONS

Part V— Effect of Dilution on the Mutual Coagulation of Colloidal Solutions of Ferric Hydroxide and Thorium Hydroxide by Prussian Blue

By

P. M. Barve, R. B. Naimpally and B. N. Desai

FROM a study of mutual coagulation of +vely charged ferric hydroxide, thorium hydroxide and ceric hydroxide by —vely charged prussian blue, copper ferrocyanide and zinc ferrocyanide sols [1, 2, 3, 4] it has been shown that the width of the zone of mutual coagulation is minimum when the charge on the colloidal particles of the reacting sols is maximum and that this relationship is independent of the fact whether the peptising electrolytes and other impurities present in the sols chemically react or not on mixing them. It has been observed by Desai and coworkers[5] that on diluting colloidal solutions of ferric hydroxide, thorium hydroxide and prussian blue, the charge on the particles first increases, reaches a maximum and then decreases for samples dialysed for periods shorter than that corresponding to the maximum in the cataphoretic speed-dialysis curve, while it continuously decreases for samples dialysed for periods equal to or longer than that period. With a view to test the validity of the conclusion arrived at earlier that the width of the zone of mutual coagulation is minimum when the charge on the particles of the reacting sols is maximum, it was decided to study the mutual coagulation of colloidal solutions of ferric hydroxide and thorium hydroxide by prussian blue by taking samples of sols dialysed and diluted to different equivalent extents.

Experimental

The sols were prepared in the same manner as before. By a number of preliminary experiments the concentrations of the colloidal solutions and the rate of their dialysis were fixed up in such a way that both the interacting colloids could have comparative (1) coagulating concentrations and (2) purity. Sols of different dilutions were prepared by adding the requisite amounts of conductivity water to the original sols. Dilution has been expressed in terms of the ratio

$$\frac{\text{volume of the diluted sol}}{\text{volume of the original sol}},$$

the original sol has thus dilution 1.

The cataphoretic speed (cat. speed) was also determined as before. In the tables of results cat. speed has been corrected for viscosity and expressed in centimetres per second per volt per centimetre $\times 10^5$.

The zone of mutual coagulation was determined exactly in the same manner as described in our last paper[1] on the subject of mutual coagulation.

All the experiments were carried out at a temperature of 30°C.

RESULTS AND DISCUSSION

The results of measurements of charge are given in Tables I and II and of mutual coagulation in Tables III and IV.

TABLE I

Changes in cataphoretic speed of colloidal solutions with progress of dialysis.

Days of dialysis	Cataphoretic speed $\times 10^5$		
	Ferric hydroxide	Thorium hydroxide	Prussian blue
0	28.5	31.2	27.4
4	37.5	36.8	31.4
8	50.3	40.4	39.0
12	67.2	44.3	43.4
16	80.5	47.7	48.5
20	51.8	35.4	36.9
24	32.3	30.8	32.8

From Table I it will appear that with the progress of dialysis the cat. speed has first increased and then decreased as is to be expected.[5] The maximum value of charge has occurred at a stage of dialysis of about 16 days in all the cases. In view of this fact, measurements of charge on dilution of the colloidal solutions were made only with two samples dialysed for periods (10 and 4 days) less than and two other samples dialysed for periods (20 and 24 days) longer than 16 days, *i.e.*, the periods before and after the maximum charge on colloidal particles is reached, because the former two samples should show as observed by Desai and co-workers[5] a first increase and then a decrease and the latter two a continuous decrease in charge with the progress of dilution of the sols. This expectation is supported by the results given in Table II.

TABLE II

Changes in cataphoretic speed of colloidal solutions dialysed to different extents on dilution.

Dilution	Cataphoretic speed $\times 10^5$											
	Ferric hydroxide— Period of dialysis in days				Thorium hydroxide— Period of dialysis in days				Prussian blue— Period of dialysis in days			
	0	4	20	24	0	4	20	24	0	4	20	24
1	28.5	37.5	51.8	32.3	31.2	36.8	35.4	30.8	27.4	31.4	36.0	32.8
2	39.6	41.8	48.5	30.8	35.8	38.4	33.3	27.5	32.5	33.6	34.6	30.6
4	37.5	45.4	46.0	28.4	33.2	41.6	31.2	25.2	30.4	35.2	32.2	28.8
6	35.4	43.2	44.3	26.1	31.2	38.1	28.6	23.4	29.8	33.1	28.4	25.7
8	33.7	41.6	40.3	26.1	30.4	35.4	25.4	21.3	28.4	30.8	25.5	22.4
10	31.8	38.3	37.5	25.9	28.6	33.2	22.6	20.4	27.1	28.7	22.8	20.8

TABLE III

Mutual coagulation of ferric hydroxide sol by prussian blue.

Numbers in different columns refer to c.c. of ferric hydroxide in 10 c.c. of the mixture of ferric hydroxide and prussian blue.

A = Appearance of turbidity. Z = Zone of coagulation. D = Disappearance of turbidity.

Dilution	Days of dialysis of ferric hydroxide and prussian blue																				
	1			4			8			12			16			20			24		
	A	Z	D	A	Z	D	A	Z	D	A	Z	D	A	Z	D	A	Z	D	A	Z	D
1	1.0	6.4	7.4	1.2	6.2	7.4	1.4	4.7	6.1	0.8	4.2	5.0	3.0	0.4	3.4	0.4	6.8	7.2	0.5	7.8	8.3
2	1.3	6.0	7.3	1.3	5.8	7.1	1.6	4.4	6.0	1.0	3.9	4.9	3.1	0.2	3.3	0.6	6.5	7.1	6.7	7.3	8.0
4	1.4	5.6	7.0	1.4	5.4	6.8	1.7	4.2	5.9	1.2	3.4	4.6	3.2	0.1	3.3	1.0	6.0	7.0	0.8	6.2	7.0
6	1.6	5.2	6.8	1.7	4.8	6.5	1.9	3.9	5.8	1.4	2.6	4.0	3.95	0.05	4.0	1.3	5.3	6.6	1.1	5.7	6.8
8	1.7	4.0	5.7	1.8	3.8	5.6	2.4	2.8	5.2	1.8	2.4	4.2	No	ppt.		1.5	5.0	6.5	1.5	5.5	6.9
10	1.9	3.7	5.6	2.0	3.5	5.5	2.5	2.5	5.0	3.6	0.8	4.4	No	ppt.		1.7	4.3	6.0	1.6	5.1	6.7
12	2.0	2.6	4.6	2.6	1.3	4.9	3.4	0.8	4.2	3.8	0.4	4.2	No	ppt.		1.8	3.3	5.1	1.8	4.6	6.4

TABLE IV

Mutual coagulation of thorium hydroxide by prussian blue.

Numbers in different columns refer to c.c. of thorium hydroxide in 10 c.c. of the mixture of thorium hydroxide and prussian blue.

A = Appearance of turbidity. Z = Zone of coagulation. D = Disappearance of turbidity.

Dilution	Days of dialysis of thorium hydroxide and prussian blue																				
	0			4			8			12			16			20			24		
	A	Z	D	A	Z	D	A	Z	D	A	Z	D	A	Z	D	A	Z	D	A	Z	D
1	1.3	5.1	6.4	1.1	3.9	5.0	1.1	3.2	4.3	2.0	3.0	5.0	2.1	1.0	3.1	1.3	3.9	5.3	1.1	5.4	6.5
2	1.5	4.9	6.4	1.1	3.8	4.9	1.3	3.0	4.3	2.3	2.5	4.8	2.0	0.9	2.9	1.6	3.6	5.2	1.7	4.9	6.6
4	1.3	4.6	5.9	1.2	3.5	4.7	1.4	2.8	4.2	2.4	2.3	4.7	2.2	0.7	2.9	1.7	3.2	4.9	1.8	4.6	6.4
6	1.6	4.3	5.9	1.4	3.3	4.7	1.7	2.3	4.0	2.5	2.0	4.5	2.4	0.4	2.8	2.0	2.7	4.7	2.0	4.1	6.1
8	1.7	4.2	5.9	1.6	3.0	4.6	1.9	2.0	3.9	2.7	1.7	4.4	2.5	0.2	2.7	2.3	2.3	4.6	2.1	3.6	5.7
10	1.8	3.7	5.5	1.7	2.8	4.5	2.0	1.8	3.8	2.9	1.3	4.2	2.6	0.1	2.7	2.4	2.2	4.2	2.3	3.3	5.6
12	2.0	3.4	5.4	1.8	2.5	4.3	2.2	1.3	3.5	3.0	1.0	4.0	No.	p pt		2.6	1.5	4.1	2.5	3.0	5.5

It will appear from the results given in Tables III and IV that the width of the zone of mutual coagulation is minimum (values of Z in the horizontal rows) for original as well as diluted sols for those samples which have been dialysed for 16 days and have maximum charge, thus confirming the earlier results [1, 2, 3, 4] and can be explained in the same manner.

The width o f the zone of mutual coagulation on diluting all the samlpe-. of the sols (values of Z in vertical columns in Tables III and IV) contisnuously decreases whether they are dialysed for short or long periods For ferric hydroxide and prussian blue dialysed for 16 days (Table III) the width of the zone of mutual coagulation for dilution 6 is very narrow, *i.e.*, only 0.05 ; it was not possible to detect the zone at great dilutions as it was too difficult to detect a width of the zone smaller than 0.05. In the case of the pair thorium hydroxide and prussian blue this difficulty was experienced only for dilution 12. It has been mentioned before that for sols dialysed for periods less than 16 days the cat. speed first increases and then decreases on dilution (Table II), while it continuously decreases for sols dialysed for periods longer than that period. Thus we find that for short period dialysed sols although the charge first increases and then decreases on dilution, the width of the zone of mutual coagulation continuously decreases, while for long period dialysed sols both the charge and the width of the zone of mutual coagulation decrease on dilution. The observation made before that the width of the zone of mutual coagulation is minimum when the charge is maximum is not supported by the present results.

Let us now examine the causes of the peculiar behaviour on dilution of the colloidal solutions. As a result of dilution the distance between colloidal particles increases and therefore the chances of collision giving rise to floculation or mutual absorption of colloids decrease. To increase the chances of collision the amount of the oppositely charged colloid will have to be increased. The same thing will also happen with reference to the other colloid. This will naturally result in narrowing down the zone of mutual coagulation on dilution, which has been also observed in the present case. It thus appears that of the two factors (1) the increase in distance on dilution and (2) charge, the influence of the first factor on the width of the zone of mutual coagulation is so predominant that it does not allow the influence of the other to be noticed at all.

SUMMARY

Mutual coagulation of +vely charged ferric hydroxide and thorium hydroxide by —vely charged prussian blue dialysed for different equivalent periods from the point of view of variation of charge on the particles, has been studied with progressive dilution of the colloidal solutions. It is observed that the conclusion that the greater the charge on the particles, the smaller the width of the zone of mutual coagulation arrived at previously is not supported by these dilution experiments as it is observed that although on dilution the charge first increases and then decreases for some samples of the sols and continuously decreases for the others, the width of the zone of mutual coagulation decreases continu-

ously. These results are explained on the basis that the effect of increasing the distance between the colloidal particles on dilution on the width of the zone of mutual coagulation is so predominant that the effect of the changes in charge is not allowed to be noticed.

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PHYSICAL CHEMISTRY LABORATORY,
WILSON COLLEGE,
BOMBAY

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AN ALKALIMETRIC METHOD OF ESTIMATION OF CADMIUM AND ZINC

By

M. M. TILLU AND M. S. TELANG

IN continuation of our previous communication "A note on the alkalimetric method of estimation of cadmium," (Tillu and Telang, J. Indian Chem. Soc., Industrial & News Edition, 1942, *5*, 134), we have made a more detailed study of the estimation of not only cadmium but also zinc whether present both together or as single cations. Cadmium is estimated after precipitation as its hydroxide, while zinc is precipitated as its carbonate, washed free from the excess of the precipitant, then treated with a concentrated solution of potassium iodide and the liberated alkali is titrated against a standard acid. The reaction is :—

$$ZnCO_3 + 2KI \rightleftarrows ZnI_2 + K_2CO_3$$

$$ZnI_2 + 2KI = K_2ZnI_4$$

EXPERIMENTAL

Estimation of Zinc :—

A stock solution of zinc chloride was prepared by dissolving a known quantity of pure zinc oxide in hydrochloric acid and then diluting to a known volume. Known portions of this solution were treated with a solution of sodium bicarbonate till no more precipitation took place and then heated in a boiling water bath for about half an hour in order to make the precipitate settle down clearly. It was then washed with hot water through a sintered glass funnel (G_3) applying suction and finally transferred into the funnel. The washings were tested with silver nitrate to free from chlorides and carbonates.

Care is to be taken that the precipitate is not allowed to be dried up in the funnel forming a cake-like mass. If this is once formed, it is difficult to make it go into solution during subsequent titrations. Further, it is preferable to precipitate the carbonate of zinc by means of sodium bicarbonate to sodium carbonate. In the latter case, the precipitate does not easily settle down and secondly, great care is necessary to prevent the excess of sodium carbonate in which the precipitate is somewhat soluble. By performing an independent experiment, we have found that using sodium bicarbonate as the precipitant and weighing as zinc oxide gives quite accurate results.

The wet and purified precipitate of zinc carbonate is then completely transferred using a wash bottle into an Erlenmeyer flask with a suitable rubber or glass stopper. A few crystals of potassium iodide are then added and vigorously shaken. The liberated alkali is then titrated against standard hydrochloric acid using methyl orange as the indicator. It is to be noted that the precipitate does not dissolve apparently in the beginning, all the same, the titration is to be carried out with the turbid solution, the solution getting completely clear towards the end of the titration as indicated by methyl orange. The factor for calculation is : 1000 c.cs. of one Normal acid is equivalent to 32.69 gms. of zinc.

Estimation of Cadmium and Zinc in their mixtures :—

In another series of experiments, known mixtures of zinc and cadmium chlorides were estimated by this method. In such mixtures, cadmium was precipitated as its hydroxide using an excess of sodium hydroxide, zinc remaining in the solution as the zincate. Then it was filtered and washed with hot water through a filter-paper (Whatman No. 1), the filtrate containing zinc. The washings were tested free from alkali as indicated by phenolphthalein. Cadmium hydroxide was estimated by the alkalimetric method. The filtrate containing the zinc and alkali was then neutralized with hydrochloric acid and concentrated to a smaller volume and the zinc was estimated by the above method.

The advantage of this method of separation is that cadmium when mixed with zinc can be quantitatively separated and estimated rapidly and accurately, employing a small number of operations. In the following table the mean results of three different experiments are recorded.

RESULTS

Oxide of	Taken	Found
Cadmium	0 1003 gms	0 0997 gms
Zinc	0 2298 gms.	0.2286 gms

Mixture of Zinc and Cadmium	Zinc Oxide		Cadmium Oxide	
	Taken	Found	Taken	Found
1	0.2298 gms.	0 2287 gms	0.1003 gms.	0.0995 gms.
2	0.1149 gms.	0.1142 gms	0.1003 gms.	0.0999 gms.
3.	0.1149 gms.	0.1141 gms.	0.1505 gms.	0.1497 gms.

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DEPARTMENT OF CHEMISTRY,
RAMNARAIN RUIA COLLEGE,
BOMBAY

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DIPOLE MOMENTS AND MOLECULAR STRUCTURE

Part III—Dipole Moments of Diethyl Esters of Substituted Malonic Acids

By

N. L. PHALNIKAR

THORPE and Ingold (J., 1915, 1080, *ibid*, 1921, 305 ; *et. seq.*) postulated the valency deflexion hypothesis to account for the failure of Baeyer's strain theory (Ber., 1885, *8*, 2277) even in the case of simple ring systems. Considerable amount of evidence has been collected in its favour from physico-chemical investigations. These methods comprise (*i*) determination of the heats of formation of 3, 4, 5 membered rings; (*ii*) determination of the relative ease of fission of spiro-compounds and the stability of ring compounds; (*iii*) hydrolysis of esters, imides and anhydrides of substituted malonic, succinic and glutaric acids; (*iv*) dissociation constants of substituted malonic, glutaric and cyclic 1 : 1 dicarboxylic acids.

Eucken and Meyer (Physikal Z., 1929, *30*, 397) and Smyth (Dielectric constant and molecular structure) have shown that the moment of a carbethoxy group for a given temperature is constant and the size of the hydrocarbon radical makes little or no difference in the magnitude of a moment of a mono-carboxylic ester. On the basis of these observations, it is expected that any change in the angle between the carbethoxy groups in a series of dicarboxylic esters must correspondingly affect the resultant moment due to the carbethoxy groups.

Accordingly, Farmer and Wallis (J.C.S., 1933, 1304) have determined the dipole moments of cyclic 1 : 1 dicarboxylic esters with a view to find further support to the valency deflexion hypothesis. Their results are inconclusive and they do not give the details of the method used by them for calculating the resultant moments.

In the present work we have determined the dipole moments of diethyl esters of substituted malonic acids and they have been discussed in relation to the valency deflexion hypothesis.

EXPERIMENTAL

Preparation of esters.—Diethyl dimethyl-malonate was prepared according to the method of Owen, Simonsen and Ramage (J.C.S., 1938, 1213). Diethyl mono-iso propyl-malonate and diethyldi-n-propylmalonate were obtained by the alkylation (mono or di as the case may be) of diethyl malonate. The crude esters in all cases were hydrolysed and the acids obtained were purified by crystallisation and again reesterified. Physical properties of the esters are summarised in the following table :—

TABLE. I

Ester	B. P.	Density at 30	Refractive Index at 30
Diethyl dimethyl malonate	195-96 (196)	0.9920	1.4010
Diethyl diethyl malonate	225-226 (230)	0.9643	1.4185
Diethyl di-n-propyl-malonate	248-50 (248-49)	0.8980	1.4169
Diethyl mono iso-propyl malonate	214 (215-6)	0.9785	1.4159

The b.p. given in the brackets have been taken from the Dictionary of organic compounds by Heilbron.

The physical constants given in this table agree with the values given in the literature.

Determination and calculation of dipole moments.—The apparatus and the method of calculation have been described in part I (J. Univ. Bom., 1941, Vol. X, Part 3, 49) and Bhide and Bhide (J. Univ. Bom., 1938, Vol. VII, Part 3, 93). The following table gives the values of the constants α and β of Hedestrand's formula (Z. Physik. Chem., 1929, B2, 428) and the polarization at infinite dilution (P_1^{∞}), the electron polarization (P_E) and the dipole moments (μ) in debye units. (The accuracy in the measurements of dipole moments is within one per cent) :—

TABLE II

Ester	α	β	P_1^{∞}	P_E	μ
Diethyl dimethyl malonate	2.9555	0.29462	185.57	46.95	2.32
Diethyl diethyl malonate	2.3598	0.2809	145.48	56.50	2.10
Diethyl di-n-propyl malonate	2.5927	0.07717	168.28	75.26	2.15
Diethyl mono-iso-propyl malonate	3.1760	0.3024	167.65	51.79	2.40

DISCUSSION

In calculating the dipole moments of substituted malonates the moment of the carbethoxy group must be known, then the resultant moment of the substituted malonates can be calculated by vector addition. Smyth and Walls (J.A.C.S., 1931, 527) and Farmer and Wallis (*loc. cit.*) assume the moment of the carbethoxy group to be 1.9 as it is the mean of Smyth and Walls values for the moment of ethyl acetate and ethyl formate. In the following calculations the mean of various values of the moment of ethyl acetate in benzene solution (1.835) has been chosen because ethyl acetate is more akin to malonates. The value of the moment of ethal acetate in benzene solution is preferred to that in the gaseous phase because the experimental determinations have been carried out in benzene solution. No correction for atom polarisation has been made.

A calculation of the dipole moments of substituted malonates can be made on the following assumptions :-

(1) The values of the intervalency angle of the middle carbon atom in substituted malonates have been taken as those calculated by Ingold and collaborators (*loc. cit.*).

(2) The moment of the carbethoxy group does not act on the C-C axis but makes an angle of 80° approximately with the C-C axis (*cf.* Bhatkhande, Phalnikar and Bhide, J. Univ. Bom. 1941, Vol. X, Part 3, 55.)

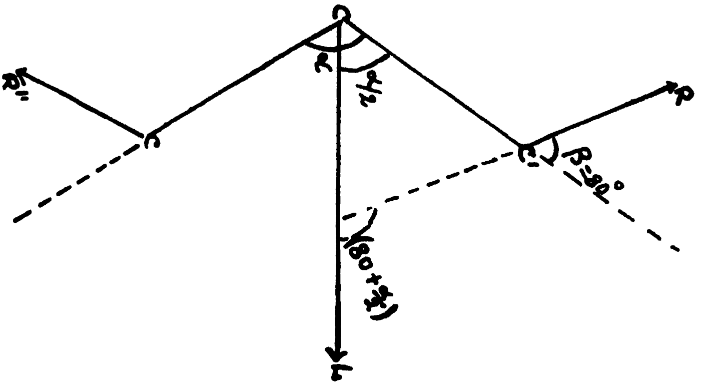
(3) Absence of rotation of the carbethoxy group about the C-C axis.

(4) Due to the interaction of the dipoles of the two carbethoxy groups they are farthest apart from one another (*i.e.*, Trans position with respect to one another).

(5) Both the dipoles act in the same plane as a result of the interaction of the dipoles.

The assumption that there is absence of rotation of the carbethoxy group about the C-C axis is justified because Smyth (*loc. cit.*) has pointed out that the moments of ethyl acetates and formates determined at different temperatures do not show any marked variation. From the dipole moments and Raman spectra of ethyl carbonate Kubo and collaborators (Sci. Papers, Inst. Phys. Chem. Res. Tokyo, 1936, *30*, 169, and 1937, *32*, 129) have shown that in this ester there is no rotation. Moreover we know that even for a simple molecule like ethane (Howard, J. Chem. Phys., 1937, *5*, 451) the rotation is very far from complete, and hence rotation, if at all present in these esters, may be assumed to be negligible.

The resultant moment due to the two carbethoxy groups can then be calculated in the usual way as will be seen from the following figure :—



	Moment along C'R'	Moment along C''R''
Component ‖ to CL	$m \cos\left(80+\frac{\alpha}{2}\right)$	$m \cos\left(80+\frac{\alpha}{2}\right)$
Component $\perp^{lar}$ to CL	$m \sin\left(80+\frac{\alpha}{2}\right)$	$-m \sin\left(80+\frac{\alpha}{2}\right)$

Components $m \sin\left(80+\frac{\alpha}{2}\right)$ and— $m \sin\left(80+\frac{\alpha}{2}\right)$ cancel each other

∴ Total resultant moment $(\mu) = 2\,m \text{ Cos}\left(80+\frac{\alpha}{2}\right) = 2\,m \text{ Cos}\left(\beta+\frac{\alpha}{2}\right)$

Fig. 1.

where, α = is the intervalency angle;

β = the angle that the moment makes with the C-C axis;

m = the moment of the carbethoxy group (1.835).

The total moment (μ) then will be equal to 2m cos $\left(\beta+\frac{\alpha}{2}\right)$.

The following table gives the results thus calculated for malonates along with the observed moments.

TABLE III

Ester	Angle	μ cal.	μ obs.	Difference
Diethylmalonate	115°, 20'	2.72	2.54	0.18
Diethyldimethyl malonate	109°, 28'	2.58	2.32	0.26
Diethyldiethyl malonate	105°, 20'	2.49	2.1	0.39
Diethyldi-n-propyl malonate	less than 109°, 28'	..	2.15	..
Diethyl mono-iso-propylmalonate	less than 115°, 20'	..	2.40	..

It will be seen from the above table that the calculated values of the moments are all higher than the observed moments. This may be due to induced moments. The order of the calculated moments, however, is the same as that of the observed moments and hence the results favour the valency deflexion hypothesis.

The observed value of the moment of diethyl-mono-isopropyl malonate is 2.4, which lies between the values of the moments of diethyl dimethyl malonate and diethyl malonate. This shows that the angle here is less than 115,20′ but greater than 109, 28′. In the case of diethyl di-n-propyl malonate the observed moment is 2.15 practically the same as that of diethyl diethylmalonate and the intervalency angle, therefore, must be 105,20′. These results are in agreement with the valency deflexion hypothesis.

Similarly the moments of cyclic 1 : 1 dicarboxylates investigated by Farmer and Wallis (*loc. cit.*) have been calculated using the above formula and are given in the following table along with the observed moments :—

TABLE IV

Ester	Angle	μ cal.	μ obs.	Difference
Diethylcyclopropane dicarboxylate	116,54′	2.75	2.4	0.35
Diethylcyclo-butane dicarboxylate	113	2.66	2.22	0.44
Diethylcyclo-pentane dicarboxylate	109,42′	2.59	2.14	0.45
Diethylcyclo-hexane dicarboxylate	107,12′	2.53	2.23	0.30

It will be observed that but for the value of the moment of diethyl cyclohexane dicarboxylate the observed moments are in the same order as that of the calculated and thus support the valency deflexion hypothesis.

SUMMARY

(1) The moments of diethyl esters of substituted malonic acids and cyclic 1 : 1 dicarboxylic acids have been calculated and have been compared with the observed moments.

(2) The results have been shown to be in accordance with the valency deflexion hypothesis.

I take this opportunity to thank Prof. B. V. Bhide for guidance in this work and for providing facilities. I also thank Dr. K. S. Nargund, Gujrat College, Ahmedabad, for the interest he took in the progress of this work and Mr. M. K. Paranjpe of the Physics department for his help in the work.

MAHARAJA PRATAPSINH CHEMICAL LABORATORY,
SIR PARASHURAMBHAU COLLEGE, POONA
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DIPOLE MOMENTS AND MOLECULAR STRUCTURE

Part IV—Dipole Moments of Glyptals

By

N. V. SATHE, N. L. PHALNIKAR AND B. V. BHIDE

GLYCERINE and phthalic anhydride form a series of complex esters having different molecular weights depending on the time of reaction. When the molecular weights of these esters become sufficiently high, products of considerable industrial importance known as Glyptal-resins are formed. Kienle, Meulen and Petke (J.A.C.S. Vol. *61*, 2258, 1939) have studied their properties. On the basis of their results they have ascribed suitable structures for the products.

These authors have established a relationship between the acid-value and molecular weights of the resin formed. They have calculated out molecular weights according to the structures given. Their calculation of molecular weights 480, 488, for resins of acid-value 235 and 190 respectively appear to be incorrect. Revised calculations give 620.6 and 788 as the molecular weights respectively. The molecular weight of the simplest resin formed from 2 mols. of glycerine and 3 mols. of phthalic anhydride should be 628 less the amount of water formed in the reaction ; since the observed molecular weights of resins of acid value 235 and 190 are also 425 and 482 respectively, it is clear that a resin of this type must contain considerable amount of unreacted glycerine and phthalic anhydride. In this investigation the dipole moments of resins of different molecular weights have been determined using dioxan as solvent, as these resins are comparatively easily soluble in this solvent.

EXPERIMENTAL

Preparation of Resins.—The resins were prepared according to the method of Kienle and co-workers (*loc. cit.*). The acid-value was used to estimate the molecular weights. Dioxan, used as solvent, was purified according to the method of K. Hess and H. Frahm (Ber. *71*, II B, 2627, 1938).

Determination and Calculation of Dipole Moments.—The apparatus and the method of calculation have been described in Part I (Phalnikar, Nargund and Bhide, J. Univ. Bom. Vol. X, Part 3, 49, 1941, and Bhide and Bhide, J. Univ. Bom. Vol. VII, Part 3, 93, 1938).

Discussion of Results.—The following table (No. I) gives the specific polarisations at various dilutions and the dipole moment of a resin of molecular weight 1048 and acid-value 128.4. The moments have been measured at five different frequencies, *i.e.*, from 30 to 300 m.

TABLE I

Specific Polarisations

Molecular Weight 1048 Acid Value 128.4

Wave length in meters	15%	10%	5%	μ
30	1.1422	1.1889	1.2522	7.37
60	1.1320	1.1751	1.2345	7.31
90	1.1049	1.1622	1.3002	7.21
160	1.0554	1.1026	1.1633	6.93
300	1.0445	1.0960	1.1556	6.88

(All dipole moments are expressed in Debye Units)

The results show that the moments increase with increasing frequency and at 150 meters anomalous dispersion is observed. Hence the rest of measurements have been carried out at a wave-length of 300 m.

The following table (No. II) gives the values of the constants α, α', (for refractive index), β of Hedestrand's formula (Z. Physikal Chem· B 2, 428, 1929), polarisation at infinite dilution (P_{I}^{α}), electron polarisation (P_{E}^{α} —) and dipole moments of different resins.

TABLE II

Resin No.	Acid Value	Molecular Weight	α	α'	β
1	214.6	430	1.1206	0.08714	0.13295
2	190.0	470	1.3591	0.09481	0.14473
3	151.6	627	18.9688	1.27326	1.91663
4	131.7	950	26.9993	1.83405	2.85116
5	128.4	1048	29.8865	2.12574	3.13006

TABLE II—*contd.*

Resin No.	Acid Value	Molecular Weight	P_1^{α}	P_E^{α}	$\ddot{\mu}$
1	214.6	430	175.42	106.25	1.85
2	190.0	470	196.06	116.13	1.90
3	151.6	627	760.32	154.68	5.48
4	131.7	950	1097.8	232.41	6.55
5	128.4	1048	1214.7	260.04	6.88

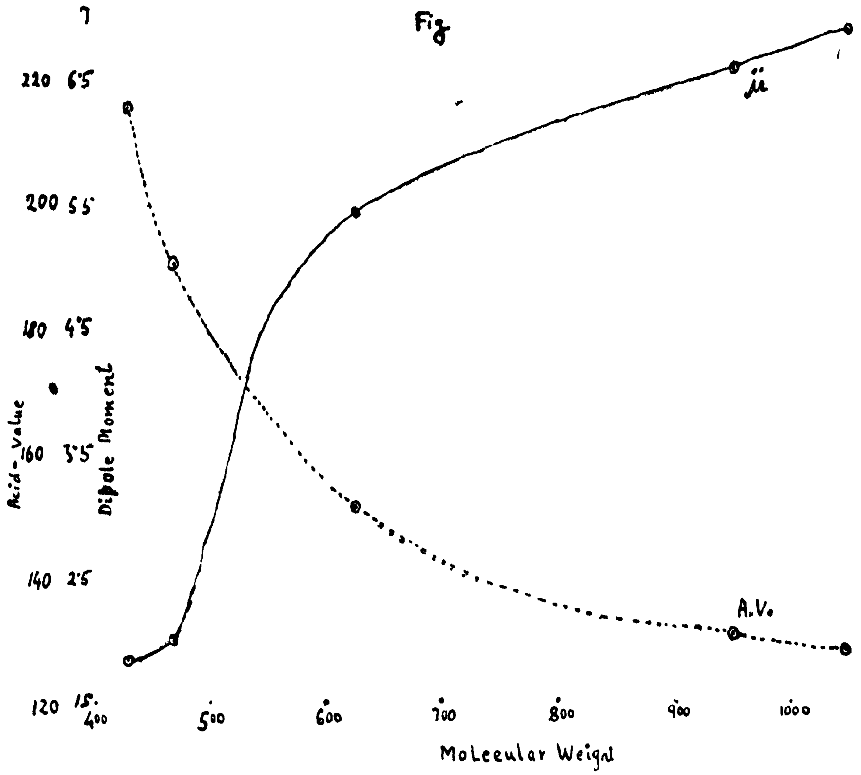

Fig. 1.

The results are represented in Fig. 1. It will be observed that the dipole moment increases with increasing molecular weight of the resin. Molecular weight of 950 indicates a limit after which the moment does not increase appreciably with increasing molecular weight.

It has been shown that the resins are mixtures consisting of monomer, dimer, trimer, tetramer, unreacted phthalic anhydride and glycerine. It is not possible, therefore, to calculate out the dipole moments from structural knowledge. It will be interesting, however, to note that when the dipole moments are plotted against molecular weight obtained from the acid-value data, a curve very similar (but inverted) to the acid-value molecular weight curve is obtained, and hence the dipole moments may be used for the determination of molecular weights of these resins. Further it will be noted that as the molecular weight increases the dipole moment of the resin appears to reach a limiting value. This may be possibly due to the formation of cross-links and as the polymerisation proceeds the molecules get larger and hence increase in length cancels out the dipole moments of the newly added groups.

From the curve in Fig. 1 it appears that more measurements of dipole moments are necessary to draw more definite conclusions, but as dioxan became unavailable experiments could not be carried out further. It was intended to find out the moment at the stage of gelation, but at this stage the solubility of the resin in dioxan became so low, that it was not possible to determine the moments.

MAHARAJA PRATAPSINH CHEMICAL LABORATORY,
SIR PARASHURAMBHAU COLLEGE, POONA

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CATALYTIC DECOMPOSITION OF POTASSIUM CHLORATE

By

G. B. KOLHATKAR AND U. A. SANT

PART I

Decomposition of potassium chlorate heated in the presence of the following oxides is studied : TiO_2, Cr_2O_3, MnO_2, Co_2O_3, Ni_2O_3 and CuO

INTRODUCTORY

DECOMPOSITION of $KClO_3$ heated alone or with other substances is studied by many workers*. When heated alone $KClO_3$ begins to decompose at about 400°C. In the neighbourhood of 400°C it mainly decomposes into $KClO_4$ and KCl and at a higher temperature, mainly into KCl and Oxygen. Teed, (J. C. S. *51* [1887] 283) suggested various equations for the decomposition of $KClO_3$. Scobai (Z. Phy. Ch. *44* [1903] 322) studied the kinetics of these reactions and Otto and Fry (J.A.C.S. *46* [1924] 269) found that the presence of KCl favours the formation of $KClO_4$.

Baudrimont (J.C.S. *24* [1871] 1151) studied the catalytic decomposition of $KClO_3$ in the presence of a number of oxides. With CuO the evolution of oxygen begins at about 240°C. At about 286°C the reaction becomes explosive, the temperature rising rapidly to 360°C and similar behaviour is shown with MnO_2. The oxygen evolved contains traces of chlorine. With Al_2O_3 the proportion of chlorine in the oxygen is a little greater. Mills and Donald (J.C.S. *4* [1882] 18) and Mills and Stevenson (*ibid* *4* [1882] 23) used ppted Fe_2O_3 and ppted MnO_2 as catalysers. With Fe_2O_3 the decomposition begins at about 190°C and with MnO_2 at about 180°C.

Hodgkinson and Lowndes (Chem. News *58* [1888] 309) and (*ibid* *59* [1889] 63) dropped MnO_2 and other oxides, well powdered, in melted $KClO_3$. A sudden evolution of oxygen occurred in many cases and the oxygen evolved contained traces of chlorine. They further found that the proportion of chlorine is greater the more acidic the oxide.

Macleod (J.C.S. *55* [1889] 184) found that the decomposition of $KClO_3$ is accelerated even when the amount of MnO used is as small as 1%. He explained the presence of chlorine in the oxygen by assuming that intermediate compounds are formed between $KClO_3$ and MnO_2 which by their decomposition produce chlorine. Sodeau (J.C.S. *8* [1902] 1066) put forth the view that the catalytic activity of the different oxides is due to their alternate oxidation and deoxidation. He suggested that the presence of chlorine in the oxygen is due to a reaction between MnO_2 and KCl. Deniges (Chem. Zentr. ii [1936] 1875) found, however, spectrospic evidence for the formation of manganese permanganate in the course of the decomposition of $KClO_3$ and MnO_2.

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* For a comprehensive summary of the previous work on this subject, see Gmelin's Handbuch Der Anorganischen Chemie, 8th Edition, Chlor, Number 6, pages 340-346.

Fowler and Grant (J.C.S. *57* [1890] 272) heated $KClO_3$ with a number of oxides and found that about 16% of the catalyst produced maximum acceleration in the decomposition.

Finely powdered silica is also found to accelerate catalytically the decomposition of $KClO_3$, Farmer and Firth (J.C.S. *25* [1924] 82).

If the temperature, at which spontaneous decomposition of $KClO_3$ occurs, in the presence of different oxides, is determined, it is found to have a definite value for each oxide, McLaughlin (J.A.C.S. *45* [1923] 1343). Further Fe_2O_3 and CuO when added to MnO_2 act as promoters and increase the catalytic activity of MnO_2, Neville (J.A.C.S. *45* [1923] 2330).

The decomposition of $KClO_3$ is found to be appreciably influenced by variations of pressure, Burrows and Brown (J.A.C.S. *48* [1926] 1790), MacLaughlin and Brown (*ibid 50* [1928] 782).

In recent years, chemical methods are supplemented by magnetic methods and they support the view that catalytic activity of MnO_2, Co_2O_3 and magnetic oxide of iron is due to the formation of unstable intermediate compounds, Bhatnagar, Prakash and Singh (J.I.C.S. *7* [1904] 125, 133), Bhatnagar Kapur, Bhatnagar and Quyyum (*ibid 8* [1941] 391).

Catalytic power of most of the oxides of the transitional elements, in the first long period of the periodic classification, has been studied by previous workers but systematic work to study the catalytic power under comparable conditions and to study the decomposition under these conditions as a time reaction has not been done. An attempt to do this is made in the present investigation.

EXPERIMENTAL

TiO_2 and Cr_2O_3 were Merck's preparations and the remaining oxides were prepared in the laboratory. All the oxides used were dried in a steam oven.

The amounts of the different oxides mixed with 122.5 gms. of potassium chlorate are :

Oxide	Amount in gms.
TiO_2	7·99
MnO_2	8.69
Fe_2O_3	7·98
Co_2O	8.29
Ni_2O_3	8.27
CuO	7·96
Cr_2O_3	7·6

Salt Used	Tem-perature**	Time in Minutes	v Volume of Gas Liberated in c.c	V Total Volume in c.c.	K	Mean K
Titanium Sulphate	275°C	20	72.0	313.4	0.00004758	
		30	96.0		0.00004697	
		40	112.8		0.00004486	
		50	128.0		0.00004406	0.00004586
Vanadium Chloride	305°C	30	43.2	329.8	0.00001524	
		60	76.0		0.00001513	
		90	102.42		0 00001518	
		120	122.42		0.00001491	0.00001511
Chromium* Sulphate	230°C	60	28.4	158.42	0.00002298	
		120	40.0		0 00001774	
		180	47.2		0 00001488	
		240	54.4		0.00001376	
Manganese Sulphate	265°C	30	30.4	313.4	0.00001142	
		60	54.8		0.00001124	
		120	94.42		0 00001147	
		180	122.82		0.00001142	0.00001138
Ferrous Sulphate	275°C	60				
		90	64.8	332 2	0.00001215	
		120	89.62		0.00001236	
		150	112.02		0 00001276	
			129.62		0 00001284	0.00001252
Cobalt Sulphate	250°C	60	32.0	329.8	0.000005428	
		120	56.0		0 000005166	
		180	78.4		0 000005252	
		240	98.42		0.000005375	
		300	115 22		0.000005428	0.000005329
Nickel Sulphate	275°C	60	49 6	313 4	0 000009997	
		120	86.42		0 00001013	
		180	114.42		0 00001020	
		240	136.02		0 00001020	0.00001013
Copper Sulphate***	275 C	60	34.4	314.0	0 000006531	
		210	62.4		0 000006585	
		180	86.12		0.000006720	
		240	106.42		0 000006803	0.000006659

* The values of the constants vary here to a considerable extent. It is probably due to the gradual oxidation of the catalyser by potassium chlorate during heating.

** The temperatures in the experiments are so chosen that about 40 per cent of the reaction should be completed in a few hours.

*** The mixtures change colour on heating and the salt cannot be extracted with water from the heated mixture. It is, therefore, probable that during heating, the salts are converted into oxides, which then act as catalysers.

N B.—Details about the investigation will be found in the thesis for M.Sc. Degree submitted to the Bombay University by V. A. Sant.

FERGUSSON COLLEGE CHEMICAL
LABORATORY, POONA

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MERCURATION OF PYRIDINE

By

C. K. KANVINDE, R. S. BORKAR, A. N. KOTHARE
AND V. V. NADKARNY

SACHS and Ebrhartinger (Ber., 1923, *56*, 2223) have described the mercuration of pyridine by heating it with mercuric acetate. They have reported the isolation of two compounds : A and B; A is obtained by adding a saturated solution of NaCl to the reaction product ; the filtrate from the above was treated with KI to give B. A was claimed to be 3, 5-dichloro-mercuri-pyridine and B to be 3-iodo-mercuri-pyridine. However, in a subsequent paper by Nial P. Macleland and Robert H. Wilson (J. C. S., 1932, 1263) the above results have been called in question. The latter authors report that A is a mixture containing 3-chloro-mercuri-pyridine (70.3 per cent) ; the other compound is not identified by them. For B, they have assigned the formula $C_5H_5NHI_3.Hg$ based on the results of analyses and on its reaction with NaOH to give yellow HgO.

Therefore, in order to remove the contradictions and clarify the position, the mercuration of pyridine has been re-investigated by us.

We have been able to obtain an amorphous powder (A) by adding saturated solution of NaCl to the reaction product of pyridine and mercuric acetate. It is found to be mixture of two substances : one of them is soluble in 95 per cent alcohol, and is found to be 3-chloro-mercuri-pyridine, with the formula $C_5H_4N.\ HgCl.\ H_2O$; on crystallisation it yields long, white needles melting at 184° C. The yield of this compound is 65 per cent. The other component insoluble in alcohol is found to be a complex compound containing two mercury atoms and two chlorine atoms with no C-Hg linkage in it. Analyses agree with the formula $C_5H_5N.\ Hg_2Cl_2$. The yield is 35 per cent.

Further, instead of NaCl solution, we have used KBr and KI solutions and obtained the corresponding compounds. Thus 3-bromo-mercuri-pyridine, 3-iodo-mercuri-pyridine and the two complex compounds $C_5H_5N.\ Hg_2\ Br_2$ and $C_5H^5N.\ Hg_2I_2$ have been isolated by us.

We have also examined the question regarding the structure of B. Our results show that the compound B is to be assigned the formula $C_5H_5\ NHI_3\ Hg$. This confirms the conclusions of the English authors. We have also been able to show that as a result of mercuration and subsequent treatment of the reaction product with KI, three different products could be isolated. They are : 3-iodo-mercuri-pyridine C_5H_4N, HgI. H_2O ; a complex of mercurous iodide and pyridine C_5H_5N. Hg_2I_2 ; and pyridine tri-iodo-mercuriate : $C_5H_5N.H.I_3Hg$.

EXPERIMENTAL

Preparation of Mercuric Acetate :—

Mercuric acetate is prepared by heating HgO with glacial acetic acid on a water bath. The heating is continued until all the mercuric oxide goes into solution. The solution is removed from the water-bath and is allowed to cool slowly, when the crystals of mercuric acetate separated from the solution. It is transferred to Buchner funnel, and the acetic acid is completely drained off by means of a suction pump. The mass is then kept over CaO in a dessicator for a few days.

Preparation of Acetoxy-Mercuri-Pyridine :—

100 gm. of mercuric acetate and 140 cc. of pyridine are mixed together in 500 cc. flask. The temperature rises to about 60°C and the mercuric acetate is dissolved. The flask is fitted with a long air condenser, and is heated on an oil bath for about 2½ hours. During the reaction the temperature is maintained between 178° and 180°. It is then allowed to cool.

3-Chloro-Mercuri-Pyridine :—

The reaction mixture is diluted with four times its volume of water and solid NaCl is added until the precipitation is complete. The mixture is filtered through Buchner funnel and dried by washing it with ether ; yield of the crude product is 152 gm. 50 gm. of the above crude product are continuously extracted with 95 per cent alcohol, in which the major part of it is found to be soluble. The remaining part is found to be insoluble in any organic solvents. It crystallises in long white needles. It melts at 184°C without decomposition. The compound obtained by the English authors melts at 278-280 with decomposition and has been given the composition C_5H_4N. Hgcl.

Found Hg=59.9% ; 59.6% ; Cl 10.5%, 10.6% ; N 4.4% ; 4.4%.

Calculated for C_5H_4N. HgCl. H_2O,

Hg. 60.4% ; N 4.2% ; Cl 10.7%.

10gm. of the substance warmed on a water bath with 5 gm. of bromine in KBr solution gave 3-bromo-pyridine. The yield of the bromo compound is 75 per cent.

3-Bromo-Murcuri-Pyridine :—

To the diluted solution of acetoxy-mercury-pyridine solid KBr is added, and the precipitate obtained is filtered through Buchner funnel. The yield of the crude product is 173 gm. 50 gm. of the above bromo-derivative are continuously extracted with 95 per cent alcohol. The alcohol extract on crystallisation yields 31.5 gm. of long white needles m.p. 148°C.

The residue insoluble in alcohol is found to be insoluble in any other organic solvent.

Found N 3.9% ; Hg 53% ; Br 21.5% ; 21.3%.
C_5H_4N. Hg Br. H_2O requires
N 3.7% ; Hg 53% ; Br 21.2%.

On bromination with bromine in KBr, 3-bromo-pyridine is obtained.

3-Iodo-Mercuri-Pyridine :—

Acetoxy-mercuri-pyridine is diluted with water, and solid KI is added in small quantities at a time till the precipitation is complete. The yield of the crude product is 212 gm. 50gm. of the above product is extracted with 95 per cent alcohol. The alcohol extract on crystallisation yields a yellow substance. The yellow substance is repeatedly treated with benzene, in which a major part of it is soluble. The benzene extract on crystallisation gives white crystalline substance which turns red in the presence of moisture.

It is fairly soluble in all common solvents. It melts at 123° without decomposition.

Found Hg 47.2% ; 47.1% ; I 30.2% ; N 3.4% ; 3.4%.
Calculated for C_5H_4N. HgI. H_2O
Hg 47.4% ; I 30.0% ; N 3.3%.

6gm. of the substance are refluxed with 100cc. of 90 per cent alcohol and 10gm. of KCl when 3-chloro-mercuri-pyridine is obtained.

Preparation of Complex Mercurous Chloride Pyridine Derivative :—

The insoluble compound obtained by treating the precipitate of chloro-derivative of mercuri-pyridine with alcohol is a gray amorphous powder, insoluble in any of the organic solvents. It decomposes at 203°—205°C.

Bromine in KBr does not substitute but decomposes the substance giving pyridine which is detected by its peculiar smell.

Found	N 2.6%;	Hg 72.2%;	Cl 12.7%.
The formula	C_5H_5N. Hg_2Cl_2 requires		
	N 2.5%;	Hg 72.7%;	Cl 12.8%.

Preparation of a Complex of Mercurous Bromide Pyridine Derivative :—

The insoluble compound, obtained from the bromo-derivative or mercuri-pyridine after extraction with alcohol is amorphous powder decomposing at 223° C. It is insoluble in organic solvents.

Found	N 2.2%;	Hg 61.8%;	Br 25.0%
The formula	C_5H_5N. Hg_2Br_2 requires		
	N 2.1%;	Hg 62.4%;	Br 25.3%.

Preparation of the Complex Mercurous Iodide Pyridine Derivative :—

The insoluble compound obtained by treating iodo-derivative of mercuri-pyridine with alcohol is found to be a gray amorphous powder insoluble in organic solvents.

It decomposes at 232°—236°C.

Found N 1.9%; Hg 54.0%; I 34.4%.
The formula C_5H_5 N. Hg_2I_2 requires
N 1.9%; Hg 54.4%; I 34.6%.

Pyridine Tri-Iodo-Mercuriate C_5H_5NH *Hg.*I_3 *:—*

1) 50 gm. of mercuric acetate and 70 cc. of pyridine are refluxed for about 2 hours on an oil-bath at 178° to 180°C. It is then diluted with water and solid NaCl is added when the precipitate of chloro-derivative of mercuri-pyridine is formed. It is then filtered. The filtrate on addition of a saturated KI solution gives a yellow precipitate. It is found to be soluble in pyridine, acetone and glacial acetic acid, but insoluble in ether and benzene. It is crystallised from glacial aceticacid. The yellow needles obtained melt at 152°—153°C. (According to the English authors, the m.p. is 154°).

Found N 2.2%; Hg 30.0%; I 57.8%.
Calculated for the formula C_5H_5NH Hg I_3
N 2.1%; Hg 30.3%; I 57.6%.

2) 50 gm. of mercuric acetate and 70 gm. of pyridine are refluxed on an oil bath heated upto 178° to 180°C for about 2½ hours.

The mixture is then diluted and a saturated solution of KI is added till the precipitation is complete. It is then filtered. The yellow precipitate is repeatedly treated with alcohol, in which the major part of the compound is soluble.

The alcohol insoluble compound is found to be complex mercurous iodide pyridine derivative C_5H_5N Hg_2I_2.

The alcohol-extract on crystallisation gives yellow needles. On heating the crystals with benzene, it is found that a large portion of them gets into solution. The soluble portion on crystallisation gives 3-iodo-mercuri-pyridine.

The benzene insoluble compound is found to be soluble in pyridine, acetone and glacial acetic acid. On crystallisation from glacial acetic acid, it forms yellow needles melting at 153°C.

It is the pyridine mercuriate C_5H_5NH Hg I_3 and shows no depression of the melting point with the compound obtained under (1) above.

SUMMARY

Pyridine has been mercurated with mercuric acetate and as the result, three different types of mercury derivatives have been obtained :

C_5H_4N. Hg X. H_2O ; C_5H_5N. Hg_2X_2 ;
and C_5H_5N. H X_3Hg.
where X=Cl, Br, I.

ST. XAVIER'S COLLEGE,
BOMBAY

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FATTY OILS FROM THE SEEDS

Of Momordica Charantia and Momordica Dioica (N.O. Cucurbitaceae)

By

J. W. AIRAN AND S. V. SHAH

THE authors (Current Science, Vol. *11*, No. *6*, 246) had reported the figures for the physical and chemical constants of these oils.

The seeds investigated were collected from the immediate neighbourhood of Kolhapur. Both these creepers grow wild, and the fruits are on the vegetable market generally during the later part of the monsoon.

M. charantia (Mar : *karla* ; Eng : *carilla fruit* ; Hindi and Gujerati : *karela*) has spindle-shaped fruit, having the appearance of crocodile's back. The fruit is bitter. The seeds are long, compressed, and are covered with red pulp when ripe.

M. dioica (Mar : *ran karla* ; Gujerati : *kantoli* ; Hindi : *beksa*) has ellipsoidal fruit, having soft spines. The seeds are biconvex, and are enclosed in red pulp when the fruit is ripe.

Both these fruits are used medicinally (M. Isaacs : Commoner Flowering Plants of Western India, 1927 Ed., pp. 145, 146) and also as vegetable ; but no particular use is indicated for the seeds alone.

The fatty oils from these seeds become rancid on exposure to the air, that from *M. charantia* being affected more quickly. In fact, when the oil from the seeds of the latter is spread in a thin layer, a white lattice-like formation is observed.

The oils were extracted with carbon tetrachloride in a soxhlet apparatus and the last traces of the solvent thoroughly removed by distillation *in vacuo*. In this solvent the oils appear red in refracted light and indicate a greenish tinge in the reflected light. Ordinarily, the oils appear greenish. They have the smell peculiar to the fruits themselves. They dissolve in petroleum ether completely. Their yields were calculated on the weight of the decorticated seeds. Table I gives their physical and chemical constants.

TABLE I

	M. charantia	*M. dioica*
Yield, per cent	35	40
Specific gravity at 25°C	0.9962	0.9892
Refractive index at 25°C	1.4985	1.5170
Acid value	4.75	2.78
Saponification value	181.3	186.6
Iodine value	73.33	72.66
Reichert-Meissel value	2.52	3.05
Polenske number	0.62	1.81
Acetyl value	2.0	7.70
Unsaponifiable matter, per cent	0.6	0.7

THE INSOLUBLE FATTY ACIDS

The oils were saponified with alcoholic potash, and the soaps, after being washed with ether, were decomposed with hydrochloric acid to liberate the fatty acids, when only in the case of the soaps from *M. charantia* a volume of greenish floculent mass appeared suspended in the beaker. When filtered through a hot water funnel, it shrank and became brown in colour. A good deal of water filtered through first, followed by brown liquid, the latter solidifying immediately. For this reason the liberated fatty acids were taken up with ether. The ether extracts were dried, and the ether removed, when brown solid masses were obtained. These solid masses, on being allowed to stand, exhibited within a short time, white flakes, apparently of stearic acid. Table II contains the constants of these mixed acids.

TABLE II

	M. charantia	*M. dioica*
Yield, per cent	93.9	90.3
Iodine value	75.71	74.76
Acid number	201.9	200.1
Hence, mean mol. wt.	277.3	279.9

Separation of saturated and unsaturated fatty acids was effected by Twitchell's lead-salt method (J. Ind. Eng. Chem., 1921, *13*, 806).

	M. charantia	*M. dioica*
Mixed acids taken	10.5 g.	13.5 g.
Solid acids obtained	1.69 g.	2.3 g
i.e., per cent	16.3	17.0
Liquid acids obtained	8.81 g.	11.2 g.
i.e., per cent	83.7	83.0

SOLID FATTY ACIDS

The solid lead salts were decomposed with dilute nitric acid, and the liberated acids taken up with ether. The ether extracts were washed with water till the washings were no longer acid to methyl orange. Then the ether was evaporated, and the solid acids obtained, crystallised from alcohol. In both cases the only saturated acid obtained was stearic acid, as can be seen from the data in Table III.

TABLE III

	M. charantia	*M. dioica*
Iodine value	1.9	2.0
Acid number	197.0	197.0
Hence, mean mol. wt.	284.3	284.3
Melting point, without any recrystallisation	65°C	65°C
Melting point, only after first crystallisation from alcohol ..	69°C	69°C

Mixed melting point with an authentic sample of stearic acid, in both the cases, was found to be 69°C.

None of the fractions during the recrystallisation yielded any other acid except stearic acid.

LIQUID FATTY ACIDS

Table IV below gives the constants of the liquid fatty acids from both these oils.

TABLE IV

	M. charantia	*M. dioica*
Iodine value	90.1	90.7
Acid number	199.2	199.7
Hence, mean mol. wt.	281.2	280.5

Bromination of these liquid acids was carried out in the usual manner in glacial acetic acid at the temperature of ice, and the mixture was left overnight in an ice-box. No solid bromine compound was obtained.

	M. charantia	*M. dioica*
Acids taken for bromination	1.8 g.	2.2 g.
Liquid bromo-compound obtained	2.93 g.	3.59 g.
Bromine contents, found, per cent	36.22	36.5

Theoretical bromine contents for Oleic Dibromide: 36.18 per cent

Thus oleic acid was found to be the only unsaturated acid present in both the oils.

In the oils, the percentages of these acids then would work out as follows :

	M. charantia	*M. dioica*
Stearic acid	15.31	15.35
Oleic acid	78.59	75.28

Thus both the oils appear to have the same fatty acid contents, their percentages varying not much. In both the cases, the stearic acid obtained is quite in pure state, whereas the so-called commercial stearic acid on the market requires several re-crystallisations to purify it.

There is another point of interest. *M. charantia* and *M. dioica* belong to a botanical natural order (*Cucurbitaceae*) the seed fats of whose members have not so far been found to contain even a preponderance of stearic acid over palmitic acid, let alone the former to the exclusion of the latter. On the other hand, the seed fats of *Luffa aegyptiaca* [Pieraerts and de Winter: Ann. Mus. Colon. Marseille, 1928, *36*, (6,) 5] and of *Trichosanthes Kadam* (Sack : Pharm. Weekblad, 1903, *40*, 313) of this same family contain about 20 per cent *palmitic* acid as the only saturated acid, and oleic acid as the only unsaturated acid.

There are, however, certain other families (*Meliaceae, Sterculiaceae, Guttiferae, Sapotaceae*, and *Verbenaceae*), the seed fats of whose members, so far investigated show a preponderance of stearic over palmitic acid, *A. floribunda* (Pieraerts and Adriaens : Mat. grasses, *21*, 8510, 8539), *A. klainei* (Adriaens : Mat. grasses, *25*, 9931, 9961), and *Garcinia Cambogia* (Rau and Simonsen : J. Soc. Chem. Ind., *41*, 902 A), all belonging to the natural order *Guttiferae*, containing stearic acid as the only saturated acid to the extent of 52-56, 65.2, and 30 per cent respectively.

There is another example where two members of the same family contain not the same saturated acid ; *Dumoria Africana* (Pieraerts : Mat. grasses, *21*, 8701) containing 46 per cent *stearic* acid and the rest oleic acid, whereas *Madhuca butyracea* (Pelly : J. Soc. Chem. Ind., *31*, 98) contains 54 per cent *palmitic* acid as the only saturated acid and the rest oleic acid. Both these belong to the natural order *Sapotaceae*.

Thus *M. charantia* and *M. dioica* seed fats, in respect of fatty acid components resemble more the seed fats from the members of these other families rather than those of its own family. As against this, they do not resemble the seed fats of the former from the point of view of the collective relative percentages of the unsaturated acids as much as they do those of their own family.

(The experimental part of this work was carried out by Mr. Airan alone.—S. V. S.)

RAJARAM COLLEGE,
KOLHAPUR

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STUDIES IN 5-HYDROXY-COUMARINS

Part I—Chalkones from 5-Hydroxy-6-Acetyl-4-Methylcoumarin

By

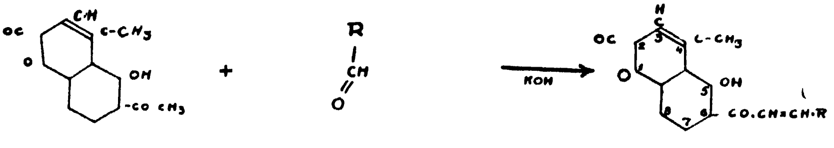
N. M. SHAH

5-HYDROXY-6-acyl-4-methylcoumarins, now easily available by the condensation of resacetophenone and several other 4-acyl-resorcinols with ethyl acetoacetate in presence of aluminium chloride (Sethna, Shah and Shah, J. 1938, 228 ; Shah and Shah, J. 1938, 1424 ; Deliwala and Shah, J. 1939, 1250 ; Proc. Ind. Acad. Sc. 1941, *13* (*A*), 352), are substances of much value for synthetical purposes. Their easy accessibility opens the way for the synthetical preparation of complex heterocyclic compounds like chromono-, flavono-, furano-coumarins and coumarones as well as natural products containing such ring-systems. As a part of the systematic study to synthesise such hetero-cyclics, this investigation has been undertaken.

The above 5-hydroxy-6-acyl-coumarins on being subjected to the Kostanecki acylation lead to the synthesis of chromono and flavono-coumarins and several of them have already been described (Sethna, Shah and Shah, *loc. cit.*, et seq). The present communication deals with the synthesis of chalkones derived from 5-hydroxy-6-acetyl-4-methylcoumarin.

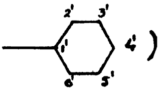
A perusal of literature shows that in recent years, a considerable amount of work on chalkones has been published (Wheeler and co-workers, J. 1937, 1737 ; 1938, 1320 et seq ; Venkataraman and co-workers, J. 1935, 866 ; 1936, 569 ; Chakravarti and Dutta, J. Indian C. S. 1939, *16*, 639 ; Lal, *ibid*, 296); but all of them are derived from aromatic ketones. No work appears to have been done on chalkones from hetero-cyclic ketone derivatives. Coumarino-chalkones described in this paper are obtained for the first time. They have been prepared from 5-hydroxy-6-acetyl-4-methylcoumarin by condensation with aldehydes, *viz.*, benzaldehyde, vanillin, β-resorcylaldehyde and anisaldehyde, protocatechuicaldehyde and salicylaldehyde in the presence of alkali. As this reaction is shown to be reversible (Schreiner and Kurosawa, J.A.C.S. 1930, *52*, 2538), the equilibrium being dependent on temperature and the concentration of the alkali, attempts were made to determine the best conditions for their preparation. The presence of the α-pyrone ring which is susceptible to rupture in presence of hot alkali further complicated the matters in the beginning. After some trials, it was observed that the above-mentioned condensation could be best effected in presence of 40-50 per cent. potassium hydroxide solution at room temperature, and that no heating should be resorted to.

The general procedure adopted was to suspend the coumarin in alcohol in which it is sparingly soluble and after addition of the aldehyde, to treat the mixture carefully with potassium hydroxide solution with cooling under tap. It was then left at room temperature with occasional shaking, the period varying with the aldehyde taken. As the reaction proceeded, the coumarin went into solution, the yellow colour being replaced by deep red-brown.



(I)

(R = any aromatic nucleus



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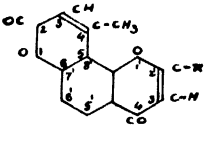
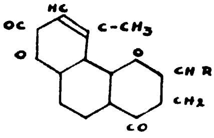


(II)



(III)

The coumarino-chalkones dissolve in conc. sulphuric acid with bluish-red colour, are soluble in alkali with yellow colour and give ferric chloride colour test.

These chalkones provide suitable starting materials for synthesis of the corresponding coumarino flavones and flavanones. 5-hydroxy-4-methyl-coumarino-6-styryl-ketone (I ; R=Ph) on treatment with selenium dioxide in amyl alcohol gave 4-methyl-flavono-7' : 8' : 6 : 5-α-pyrone (II ; R=Ph) in good yield (Shah and Deliwala, Proc. Ind. Acad. Sc., under publication) and on treatment with dilute alkali gave 4-methyl-flavanono-7' : 8' : 6 : 5-α—pyrone (III ; R=Ph).

EXPERIMENTAL

5-hydroxy-4-methylcoumarine-6-styryl-ketone:—5-hydroxy-6-acetyl-4-methyl-coumarin (Sethna, Shah and Shah, J. 1938, 228) (2.5 g.), alcohol (30 c.c.) and benzaldehyde (1.5 c.c.) were mixed and to the mixture potassium hydroxide (50 per cent. 35 c.c.) was slowly added with cooling under tap. The mixture was then left overnight with shaking at intervals. As the reaction proceeded, the insoluble coumarin went into solution, a dark red solution resulting. It was then diluted with cold water and acidified with acetic acid. A reddish oil separated which slowly solidified. The solid was collected and boiled with a little quantity of alcohol. Two isomeric chalkones were separated. The insoluble part was crystallised from acetic acid, in fine yellow needles, m.p. 221-220°. (Found : C, 74.14 ; H, 4.97. $C_{19}H_{14}O_4$ requires C, 74.5 ; H, 4.6 per cent.).

The alcohol-soluble portion deposited on keeping yellow granular crystals, recrystallised from alcohol, m.p. 175-176°.

Both the chalkones give ferric chloride colour test, dissolve in sulphuric acid with bluish-red colour and give yellow colour without any fluorescence in alkali in which it is sparingly soluble.

The above condensation was tried in presence of different concentrations of alkali : 40 per cent. KOH gave the same products ; in presence of 25 per cent. KOH, a mixture of chalkone and flavanone was produced; with 10 per cent. concentration of alkali, no condensation could be affected.

Action of dilute alkali on the above chalkones :—The chalkone m.p. 175-176° (1 g.) was treated with sodium hydroxide solution (1.5 per cent.; 15 c.c.) for about 10-15 minutes on boiling water-bath and then allowed to remain at room temperature overnight. It was then acidified and the solid obtained crystallised from alcohol, small colourless needles, m.p. 237°. 4-methyl-flavanono-7′ : 8′ : 6 : 5-α-pyrone (III ; R = Ph) is insoluble in alkali and gives no colour with ferric chloride. (Found : C, 74.2 ; H, 4.5. $C_{19}H_{14}O_4$ requires C, 74.5 ; H, 4.6 per cent.).

The chalkone m.p. 221-222° was similarly treated ; but instead of the above flavanone, the substance obtained was found to be the chalkone, m.p. and mixed m.p. 176°. This shows that both the chalkones are geometrically isomeric.

5-hydroxy-4-methylcoumarino-6-(3′-methoxy-4′-hydroxy-styryl)-ketone :—The coumarin (2.5 g.) in alcohol (40 c.c.) was mixed with vanillin (2 g.) and KOH solution (50 per cent. ; 35 c.c.) was carefully added with shaking and cooling as before. It was then left at room temperature for 60 hours, afterwards diluted with water and acidified with conc. HCl to which few c.c. of acetic acid were added. The solid separated on scratching the sides of the beaker ; it was collected after some time, washed with dil Na_2CO_3 solution and crystallised from alcohol, yellow needles, m.p. 163-164° mixed m.p. with the original coumarin depressed to 132°. (Found : C, 68.0 ; H, 4.8. $C_{20}H_{16}O_6$ requires C, 68.2; H, 4.54 per cent.).

5-hydroxy-4-methylcoumarino-6-(2′ : 4′-dihydroxy-styryl)-ketone :—The mixture of the coumarin (2 g.), alcohol (40 c.c.) and β-resorcyl-aldehyde (1.5 g.) was treated with KOH (50 per cent. 35 c.c.) as before and allowed to remain for nearly 60 hours. It was diluted and acidified with conc. HCl. The chalkone crystallised from alcohol, yellow needles, m.p. 166-167°. (Found: C, 67.21 ; H, 4.1. $C_{19}H_{14}O_6$ requires C, 67.45; H, 4.14 per cent.).

5-hydroxy-4-methylcoumarino-6-(3′:4′-dihydroxy-styryl)-ketone :—This chalkone was obtained from protocatechuicaldehyde similarly as before. It crystallised from alcohol, long yellow needles, m.p. 163°. (Found : C, 64.25 ; H, 4.63. $C_{19}H_{14}O_6 + H_2O$ requires C, 64.1 ; H, 4.6 per cent.).

5-hydroxy-4-methylcoumarino-6-(4′-methoxy-styryl)-ketone :—The coumarin and anisaldehyde in the same proportions as before were similarly kept in presence of KOH for 24 hours. The chalkone crystallised from hot acetic acid, in clusters of reddish yellow needles, m.p. 243°. (Found : C, 71.15 ; H, 4.6. $C_{20}H_{16}O_5$ requires C, 71.4 ; H, 4.76 per cent.).

5-hydroxy-4-methylcoumarino-6-(2′-hydroxy-styryl)-ketone :—This condensation using salicylaldehyde was carried out as in the previous case. The chalkone obtained crystallised from alcohol, m.p. 233° (decomp.). (Found : C, 69.87 ; H, 4.2. $C_{19}H_{14}O_5$ requires C, 70.8 ; H, 4.25 per cent.).

Attempted condensation of cinnamic aldehyde :—The condensation of cinnamic aldehyde gave a product from which no crystalline product could be isolated.

The C-H determinations are micro-analyses partly by Prof. T. R. Seshadri and partly by Dr. D. Chakravarti, to whom my thanks are offered.

The preliminary work was done with Mr. C. V. Deliwala, M.Sc., to whom I express my thanks.

In conclusion, it is a great pleasure to express my thanks to Dr. R. C. Shah for his sympathetic interest.

Further work is in progress.

THE MADHAVLAL RANCHHODLAL
SCIENCE INSTITUTE,
GUJARAT COLLEGE, AHMEDABAD

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ALUMINIUM CHLORIDE, A NEW REAGENT FOR THE CONDENSATION OF β-KETONIC ESTERS WITH PHENOLS

Part VIII—The Condensation of Resacyl-and Gallacyl-Phenones (4-Acyl-Resorcinols and Pyrogallols) Containing Long-Chain Acyl Groups

By

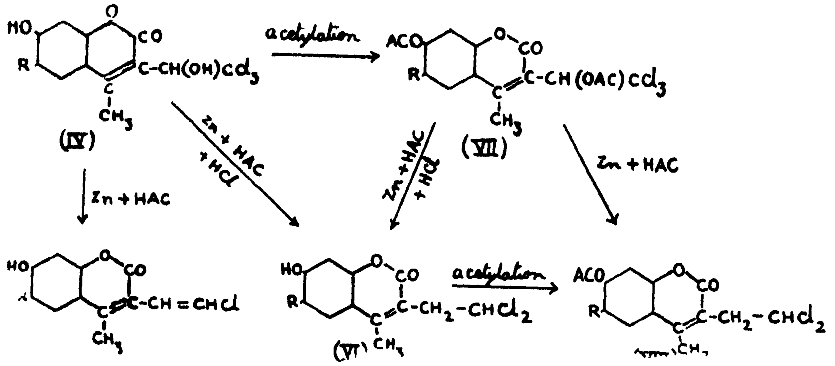
M. C. Chudgar and N. M. Shah

IN extension of the work already published in the previous parts of this series (Sethna, Shah and Shah, J. 1938, 228 ; Sethna and Shah, J. 1938, 1066 ; Shah and Shah, J. 1938, 1424 ; Deliwala and Shah, J. 1939, 1250 ; Proc. Ind. Acad. Sc., 1941, *13*(*A*), 352 ; *ibid*, 1942, and under publication), we have now investigated the condensation of ethyl acetoacetate with resacyl-phenones (4-acyl-resorcinols) containing long-chain acyl groups. In this paper is described the condensation of 4-stearyl-resorcinol and derivatives with ethyl acetoacetate in presence of anhydrous aluminium chloride.

4-stearyl-resorcinol condenses with ethyl acetoacetate in presence of aluminium chloride in dry nitro-benzene solution at 110°, giving 5-hydroxy-6-stearyl-4-methylcoumarin (I) in good yield. The constitution assigned to the condensation product is proved to be (I) by analogy with previous condensations and on the following grounds : (*i*) it gives positive ferric chloride colour test, and in alkaline solution turns deep yellow without any fluorescence characteristic of a 5-hydroxy-coumarin derivative (Collie and Chrystall, J. 1907, *91*, 1804 ; Dey, J. 1915, *107*, 1614) and (*ii*) on Kostanecki acetylation, it gives 2′:4-dimethyl-3′-hexadecyl-7′:8′:6:5-α-pyrone (II).

It may be mentioned here that 4-stearyl-rescorcinol does not condense with acetoacetic ester with sulphuric acid as condensing agent. 4-stearyl-resorcinol on Clemmensen reduction gave 4-octadecyl-resorcinol, which on Pechmann condensation with acetoacetic ester gave 7-hydroxy-6-octadecyl-4-methyl-coumarin.

5-nitro and 5-bromo-resstearo-phenones did not undergo the condensation. 4-stearyl-pyrogallol also did not condense with ethyl aceto-acetate.



The formation of 5-hydroxy-coumarin in the above condensation is in conformity with the previous results (*loc. cit.*) : the chelation between -OH and -CO. R fixes the double bonds with the stabilisation of one of Kekule forms. The reactivity in 2-position of resorcinol nucleus thus leads to the production of 5-hydroxy-coumarin derivative. The non-condensation of 4-stearyl-pyrogallol is also explicable on the above view, as the C atom marked with asterisk is not united by a double bond with C atom bearing the hydroxyl group (*vide* Shah and Shah, *loc. cit.*).

EXPERIMENTAL

Condensation of 4-stearyl-resorcinol with ethyl acetoacetate in presence of aluminium chloride : formation of 5-hydroxy-6-stearyl-4-methylcoumarin :—

4-stearyl-resorcinol was prepared by the Nencki reaction according to the procedure of Dr. R. D. Desai and Waravdekar. We thank Dr. Desai for supplying us the details recently published in the Proc. Ind. Acad. Sc.

To the solution of aluminium chloride (4 g. : 2 mols.) in dry nitrobenzene (25 c.c.), dry 4-stearyl-resorcinol (5 g. : 1 mol.) and acetoacetic ester (3 g. : 1 mol.) were added and the mixture protected from moisture by $CaCl_2$ guard-tube was heated at 110° and finally to 115° for one hour. Higher temperatures produced a dark product difficult to purify. HCl fumes were copiously evolved and when the evolution of the gas slackened, the reaction-mixture was cooled, treated with cracked ice, some conc. HCl (10 c.c.) added and nitro-benzene steam-distilled off. The brown residual oil solidified on cooling. It was titruated with little alcohol, which removed coloured impurities ; the white residue was collected and crystallised from alcohol in which it is sparingly soluble, small sandy granules, m.p. 116°, and recrystallised from hot glacial acetic acid, clusters of slender needles, m.p. 116-117° : yield, about 2 gms. (Found : C, 74.8 ; H, 9.7. $C_{28}H_{42}O_4.0.5H_2O$ requires C, 74.5 ; H, 9.54 per cent).

The *coumarin* is insoluble in aqueous alkali but turns deep yellow, and its alcoholic solution gives wine red colour with ferric chloride.

The *acetyl derivative* prepared by refluxing with acetic anhydride and a few drops of pyridine for 6 hours crystallised from alcohol and recrystallised from petroleum benzine, small needles, m.p. 98°. (Found: C, 73.24; H, 8.85. $C_{30}H_{44}O_5.0.5H_2O$ requires C, 73.04; H, 9.13 per cent).

Kostanecki Acetylation of the coumarin: Formation of 2′:4-dimethyl-3′-hexadecyl-chromono-7′:8′:6:5-α-pyrone:—

The coumarin (1 g.), acetic anhydride (10 c.c.) and fused sodium acetate (1 g.) were heated for about 11 hours at 140-150° on oil-bath under reflux. The mixture was then cooled, treated with water; a pasty mass separated; it was washed with $NaHCO_3$ solution and then with dilute NaOH. The residue was collected and crystallised from boiling alcohol, small needles, m.p. 135-136°. (Found: C, 74.98; H, 8.4. $C_{30}H_{42}O_4.H_2O$ requires C, 74.4; H, 9.1 per cent).

The chromono-α-pyrone is insoluble in NaOH and gives no colour with ferric chloride and with conc. H_2SO_4.

Condensation of 4-octadecyl-resorcinol: formation of 7-hydroxy-6-octadecyl-4-methylcoumarin:—

4-stearyl-resorcinol on Clemmensen reduction gave 4-octadecyl-resorcinol (Desai and Waravdekar, *loc. cit.*).

The octadecyl-resorcinol (1 g.), acetoacetic ester (0.5 g.) were mixed and phosphorus oxychloride (1 c.c.) added. The mixture was left overnight at room temperature. After about an hour, it began to solidify. It was treated with water and the solid crystallised from alcohol, clusters of small needles, m.p. 116-117°, mixed m.p. with 5-hydroxy-6-stearyl-4-methylcoumarin was considerably depressed. (Found: C, 78.3; H, 10.1. $C_{28}H_{44}O_3$ requires C, 78.5; H, 10.3 per cent).

The coumarin is insoluble in aqueous alkali but dissolves in alcoholic alkali with blue fluorescence. It gives no colour with alcoholic ferric chloride.

The *acetyl* derivative prepared by acetic anhydride-pyridine method (refluxing for 4 hours) crystallised from alcohol, granules; m.p. 78-79°. (Found: C, 76.3; H, 9.6. $C_{30}H_{46}O_4$ requires C, 76.6; H9.8 per cent).

Further work is in progress.

We thank Professor M. S. Shah for facilities.

In conclusion, we thank Dr. R. C. Shah for his sympathetic interest in the investigation.

THE MADHAVLAL RANCHHODLAL
SCIENCE INSTITUTE,
GUJARAT COLLEGE, AHMEDABAD

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THE REDUCTION OF -CH(OH)CCl_3 GROUP ATTACHED TO A BENZO-α-PYRONE NUCLEUS—PART II

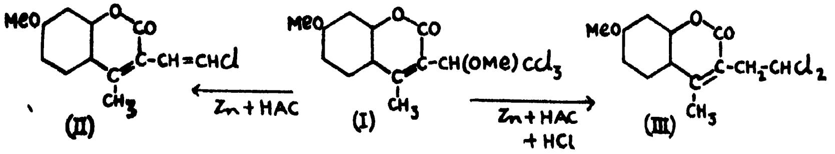
By

M. C. CHUDGAR AND N. M. SHAH

In Part I, Kulkarni and Shah (Proc. Ind. Acad. Sc., 1941, *14*(*A*), 151) from a study of the reduction of various 3-CH(OH)CCl_3-substituted coumarin derivatives showed that (*a*) on reduction with zinc and acetic acid, the group -CH(OH) CCl_3 in the pyrone ring is reduced to -CH= CHCl group in case of hydroxy-coumarins and (*b*) the same group is reduced to -CH_2. $CHCl_2$ if the reduction is carried out in conjunction with concentrated hydrochloric acid or the phenolic group is either absent or is protected by acetylation.

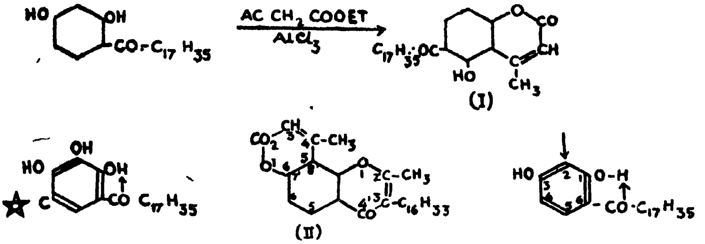
In extension of the above investigation, we have now studied the reduction of (1) 7-methoxy-3-(α-methoxy-βββ-trichloroethyl)-4-methylcoumarin, (2) 7-hydroxy-6-ethyl-3 (α-hydroxy βββ trichloroethyl)-4-methylcoumarin and its acetoxy derivative and (3) 7-hydroxy-6-butyl-3-(α-hydroxy-βββ-trichloroethyl)-4-methylcoumarin and its acetoxy derivative, the reducing agents used being the same as in the previous part.

7-Hydroxy 3-(α—hydroxy-βββ-trichloroethyl)-4-methylcoumarin (Kulkarni, Alimchandani and Shah, J.I.C.S., 1941, *18*, 115) on methylation by dimethyl sulphate in ice gave 7-methoxy-3-(α-methoxy-βββ-trichloroethyl)-4-methylcoumarin (I) which on reduction with zinc and acetic acid gave 7-methoxy-3-(β-chlorovinyl)-4-methylcoumarin (II); and on the same reduction in conjunction with conc. hydrochloric acid, 7-methoxy-3-(β-β-dichloroethyl)-4-methylcoumarin (III) was obtained.



The above results show that the reduction of the methoxy derivative takes place similar to that of hydroxy-coumarins. This is in contrast to the behaviour of acetoxy derivatives which give the reduction product containing -CH_2. $CHCl_2$ and the acetyl group is eliminated during the reduction with the production of the hydroxy derivative.

7-Hydroxy-6-ethyl-3-(α-hydroxy-βββ-trichloroethyl)-4-methylcoumarin (IV; R=Et; Shah and Kulkarni, J. Univ. Bom., 1941, *10*, 86) on reduction with zinc and acetic acid gave 7-hydroxy-6-ethyl-3-(β-chlorovinyl)-4-methylcoumarin (V; R=Et), and 7-hydroxy-6-ethyl-3-(ββ-dichloroethyl)-4-methylcoumarin (VI; R=Et) when the reduction was carried out in conjunction with conc. hydrochloric acid. The acetyl derivative (VII; R=Et) on reduction with zinc and acetic acid in conjunction with conc. hydrochloric acid also gave the same product (VI; R=Et). If the above reduction was carried out by zinc and acetic acid, 7-acetoxy-3-(ββ-dichloroethyl)-4-methylcoumarin (VIII; R=Et) was obtained, identical with the acetoxy derivative of VI (R=Et).



7-Hydroxy-6-butyl-3-(α-hydroxy βββ-trichloroethyl)-4-methylcoumarin (IV; R=*n*-butyl) behaves exactly similarly: it gave 3-(β-chlorovinyl)-coumarin derivative (V; R=*n*-butyl) and 3-(-ββ-dichloroethyl) coumarin (VI; R=*n*-butyl) when reduced without and with conc. HCl respectively. The acetoxy derivative (VII; R=*n*-butyl) on reduction with zinc and acetic acid only gave VIII (R=*n*-butyl) identical with the acetoxy derivative of the coumarin (VI), obtained directly on reduction in presence of conc. HCl of the acetyl derivative (VII; R=*n*-butyl).

The above results are in conformity with those obtained by the previous investigators (*loc. cit.*). The generalisation arrived in the previous communication also holds good in the case of the reduction products described in this paper.

EXPERIMENTAL

1. *Reduction of 7-methoxy-3-(α-methoxy-βββ-trichloroethyl)-4-methylcoumarin.*

The methoxy derivative was prepared according to Kulkarni, Alimchandani and Shah (J. I. C. S., 1941, *18*, 116).

(a) *By zinc and acetic acid: formation of 7-methoxy-3-(β-chlorovinyl)-4-methylcoumarin (II).*

The methoxy coumarin (I; 1. g.) was dissolved in glacial acetic acid (15 c.c.). Zinc dust (1 g.) was sprinkled over the solution in small instalments at a time. The mixture was occasionally shaken. When the whole of zinc was added, the mixture was boiled for about 5-7 minutes and filtered from unchanged zinc; the filtrate diluted with water, when a yellow solid separated. It was crystallised from alcohol, yellow needles, m.p. 160-161°, mixed melting point with the original coumarin was depressed to 133° : (Found : Cl, 14.14. $C_{13}H_{11}O_3Cl$ requires Cl, 14.16 per cent).

(b) *By zinc, acetic acid and conc. HCl : formation of 7-methoxy-3-(ββ-dichloroethyl)-4-methylcoumarin (III).*

To the solution of the methoxy-coumarin (I ; 1 g.) in glacial acetic acid (15 c.c.), conc. HCl (5 c. c.) was added and the mixture treated with zinc dust in small instalments as before. Vigorous reaction took place. After the addition of zinc was over, the mixture was boiled for a few minutes and then filtered. The filtrate was diluted with water ; the solid was collected and crystallised from alcohol, needles, m.p. 113-114.° (Found : Cl, 24.05. $C_{13}H_{12}O_3Cl_2$ requires Cl, 24.7 per cent).

2. *Reduction of 7-hydroxy-6-ethyl-3-(α-hydroxy-βββ-trichloroethyl)-4-methylcoumarin.*

(a) *By zinc and acetic acid : formation of 7-hydroxy-6-ethyl-3-(β-chlorovinyl) -4-methylcoumarin (V ; R=Et).*

The coumarin (IV ; R=Et) ; (Shah and Kulkarni, J. Univ. Bom., 1941, *10*, 87); (2 g.) was dissolved in hot acetic acid (30 c. c.) and zinc dust (2 g.) was added as before. The reaction-mixture was greenish in colour and exhibited blue fluorescence. It was filtered from unchanged zinc and the filtrate diluted with water. A yellowish solid separated ; it was crystallised from alcohol, yellow rhombic crystals, m.p. 238-240°. (Found : Cl, 13.2. $C_{14}H_{13}O_3Cl$ requires Cl,1 3.41 per cent).

The reduction product is soluble in hot alcohol, acetone, acetic acid and sparingly so in chloroform.

The *acetyl* derivative prepared by acetic anhydride-pyridine method crystallised from alcohol, yellowish thick needles, m.p. 191-192°. (Found: Cl, 11.44. $C_{16}H_{15}O_4Cl$ requires Cl, 11.6 per cent).

(b) *By zinc, acetic acid and conc. HCl : formation of 7-hydroxy-6-ethyl-3-(ββ-dichloroethyl)-4-methylcoumarin (VI; R=Et).*

(*i*) The coumarin (IV ; R=Et) (1 g.) was dissolved in acetic acid (20 c.c.) by heating and conc. HCl (5 c.c.) added and the reduction carried out as before and the reduction product isolated similarly. It was crystallised from alcohol, sandy granules, m.p. 253-255°. (Found : Cl, 23.43. $C_{14}H_{14}O_3Cl_2$ requires Cl, 23.6 per cent).

(*ii*) The acetyl derivative (VII ; R=Et) was reduced as in (*i*). The reduction product was isolated similarly and crystallised from alcohol. It was identical with the above product, m.p. and mixed m.p. 253-255°.

Formation of 7-acetoxy-6-ethyl-3- (ββ-dicholroethyl)-4-methylcoumarin (VIII; R=Et).

(*i*) The acetyl derivative (VII ; R=Et) was reduced by zinc and acetic acid as in the previous cases. The reduction product was crystallised from alcohol, m.p. 167°. (Found : Cl, 20.46. $C_{16}H_{16}O_4Cl_2$ requires Cl, 20.68 per cent).

(*ii*) The coumarin (VI ; R=Et) was acetylated by acetic anhydride and sulphuric acid method. The acetyl derivative crystallised from alcohol, needles, m.p. 167° and mixed with the above product, the m.p. was the same.

Condensation of 4-butyl-resorcinol with ethyl α-(α-hydroxy-βββ-trichloroethyl) acetoacetate: formation of 7-hydroxy-6-butyl-3-(α-hydroxy-βββ-trichloroethyl) -4-methylcoumarin (IV; R=n-butyl).

4-butyl-resorcinol was prepared by the Clemmensen reduction of res-butyrophenone.

The resorcinol (3 g.) and the ester (6 g.) were mixed and phosphorus oxychloride (2-3 c.c.) added with cooling under tap. The reaction mixture was left overnight and then treated with ice water: a viscous mass separated; it was left in contact with little acetic acid, when a white solid was obtained. It was crystallised from high boiling petroleum benzine and then from alcohol, m.p. 166-167°. (Found: Cl, 28.5. $C_{16}H_{17}O_4Cl_3$ requires Cl, 28.1 per cent).

The coumarin is soluble in ethyl acetate, mixture of CCl_4 and benzene and sparingly so in petroleum benzine. It shows blue fluorescence in alkaline solution.

The *acetyl* derivative prepared by acetic anhydride-sulphuric acid method, crystallised from acetic acid, white needles, m.p. 123-24°. (Found: Cl, 23.4. $C_{20}H_{21}O_6Cl_3$ requires Cl, 22.9 per cent).

3. *Reduction of 7-hydroxy-6-butyl-3-(α-hydroxy-βββ-trichloroethyl)-4-methyl-coumarin.*

The reduction of this coumarin was studied as in the previous cases, using zinc and acetic acid without and with conc. HCl. The procedure was also exactly similar. For brevity therefore, the following reduction products with their melting points and analysis are described without repeating the details:

1. *7-hydroxy-6-butyl-3-(β-chlorovinyl)-4-methylcoumarin*: needles from alcohol, m.p. 167°. (Found: Cl, 12.13. $C_{16}H_{17}O_3Cl$ requires Cl, 12. 12 per cent).

2. *7-hydroxy-6-butyl-3-(ββ-dichloroethyl)-4-methylcoumarin*: needles from alcohol, m.p. 196-197°. (Found: Cl,21.9. $C_{16}H_{18}O_3Cl_2$ requires Cl, 21.56 per cent).

3. *7-acetoxy-6-butyl-3-(ββ-dichloroethyl)-4-methylcoumarin*: needles from alcohol, m.p.156-157°. (Found: Cl, 19.05. $C_{18}H_{20}O_4Cl_2$ requires Cl, 19.12 per cent).

4. *7-acetoxy-6-butyl-3-(β-chlorovinyl)-4-methylcoumarin*: yellowish plates from alcohol, m.p. 143°. (Found: Cl, 10.5. $C_{18}H_{19}O_4$ Cl requires Cl, 10.6 per cent).

We thank Professor M. S. Shah for facilities. Our grateful thanks are expressed to Dr. R. C. Shah for his sympathetic interest.

THE MADHAVLAL RANCHHODLAL
SCIENCE INSTITUTE,
GUJARAT COLLEGE, AHMEDABAD

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LONG CHAIN ACYL AND ALKYL PHENOLS

By

MISS K. PARANJAPE, N. L. PHALNIKAR AND K. S. NARGUND

LONG chain acyl and alkyl phenols are required in this laboratory in connection with work on synthetical anthelmintics. An additional point of interest in their preparation was that a number of these long chain alkyl phenols are being recently exploited for technically important products.

There are mainly three methods for the preparation of acyl phenols which by subsequent reduction by Clemensen's method yield alkyl phenols. (1) Nencki's reaction consisting in heating together a phenol, an acid and anhydrous zinc chloride, is well known to give good yields of 4-acyl resorcinols and 2-acyl quinols when resorcinol and hydroquinone are used. The reaction, however, has been little used for the condensation of monohydric phenols except by Michael and Palmer (Amer. Chem. J. 1885, *7*, 275) who obtained p-acetyl-phenol and by Goldzweig and Kaiser (J. Pr. Chem. 1891, *43*, 86) who obtained p-propionylphenol by this reaction although the yields are not mentioned in either case. Coulthard, Marshall and Pyman (J.C.S. 1930, 280) investigated Nencki's reaction with phenol, cresols and fatty acids upto heptoic acid and found that the yields of the ketones were very low and that both ortho and para isomers were formed simultaneously. Desai and Warvadekar (Proc. Ind. Accad. Sciences, 1940, *12*, 507), studied Nencki's reaction with α-naphthol and obtained 2-acyl—naphthols. (2) Fries' transformation of phenyl esters is the next important method for the preparation of acyl phenols. It is found that both ortho and para isomers are formed in this reaction. Fries' transformation of phenyl laurate and phenyl stearate has been studied by Bell and Driver (J.C.S. 1940, 836), while that of phenyl pentadecylate by Gokhale, Patel and Shah (Current Science, 1940, *9*, 362). (3) Friedel and Crafts reaction of a phenol ether or phenol with acid chlorides is the method for getting acyl phenols (Johnson and Kohmann J.A.C.S. 1914, *36*, 1259; Auwers Ber. 1903, *36*, 3899). Ralston and Bauer (J. Org. Chem. 1940, *5*, 165), studied the Friedel and Craft's reaction of phenol with acid chlorides of heptoc, lauroic, myristic, palmitic and stearic acids and found that both ortho and para compounds were formed and that the ratio of ortho to para decreased with increase in the length of the chain.

We were interested in getting ortho and para acyl phenols in pure condition and good yields. The present communication deals with the successful attempts made in that direction. Contrary to expectation it has been found that Nencki's reaction with phenol and lauric, myristic palmitic and stearic acids gave pure ortho acyl phenols in yields over 70 per cent. Para isomers do not seem to have been formed under these conditions. The constitutions of ortho acyl phenols were determined by methylation and subsequent oxidation when o-methoxy benzoic acid was obtained. Nencki's reaction, in this case, is the best method to get ortho acyl phenols. Similarly it has been found that Friedel and Craft's reaction of anisole with acid chlorides in nitrobenzene solution gave more than 84 per cent. of para acyl anisoles which by demethylation with hydrobromic acid in acetic acid solution gave p-acyl phenols in overall yields of 80 per cent.

The experimental methods used are described in case of compounds derived from stearic acid. Similar methods were used in other cases and the compounds obtained are described in tabular form for the sake of brevity.

EXPERIMENTAL

o-Hydroxyphenyl heptadecyl ketone :—Phenol (9.4 gms.) stearic acid (28.4 gms.) and anhydrous zinc chloride (27.2 gms.) were heated together on sand bath for six hours. It was poured in water and the solid obtained was purified by washing with water and sodium carbonate solution. It was then crystallised from alcohol and then from benzene, m.p. 66-67°. Bell and Driver (*loc. cit.*) and Ralston and Bauer (*loc. cit.*) give the m.p. 64° for this substance.

o-methoxy phenyl heptadecyl ketone :—The above ketone (1 gm.), anhydrous potassium carbonate (2 gms.), dimethyl sulphate (3 cc.) and acetone (20 cc.) were heated together on water bath for six hours. It was then filtered and acetone removed. The residue was washed with a solution of sodium hydroxide to remove the unmethylated material, and then crystallised from methyl alcohol m.p. 42°. (Found : C, 79.8 ; H, 11.3 per cent; $C_{25}H_{42}O_2$ required C, 80.2 ; H, 11. . per cent). On oxidation with potassium permanganate in acetone solution it gave o-methoxy benzoic acid m.p. 101 identified by mixed m.p. with an authentic sample.

o-hydroxy octadecyl benzene :—It was obtained by the reduction of o-hydroxy phenyl heptadecyl ketone by zinc amalgam and hydrochloric acid in acetic acid solution, m.p. 58°. (Found : C, 83.8 ; H, 12.5 per cent; $C_{24}H_{42}O_1$ required C, 83.2 ; H, 21.1 per cent).

p-Methoxy phenyl heptadecyl ketone :—To a mixture of anisole (10 gms.), stearyl chloride (32 gms.) and nitrobenzene (40 gms.) was gradually added anhydrous aluminum chloride (30 gms.) A crimson red mixture was formed which was allowed to remain overnight. It was then decomposed with ice and hydrochloric acid and steam distilled to remove nitrobenzene. The residue was washed with a solution of sodium hydroxide and crystallised from methyl alcohol m.p. 75°, yield 90 per cent. (Found : C, 79.7 ; H, 11.1 per cent; $C_{25}H_{42}O_2$ requires C, 80.2 ; H, 11.2 per cent). On oxidation it gave anisic acid and on demythylation gave p-hydroxy phenyl heptadecyl ketone m.p. 90°. (Bell and Driver give m. p. 90-90.5).

p-Methoxy octadecyl benzene :—It was obtained by the reduction of the ketone by zinc amalgam and hydrochloric acid and purified by crystallisation from methyl alcohol m.p. 60°. (Found : C, 83.5 ; H, 12.3. per cent; $C_{25}H_{44}O$ requires C, 83.3 ; H, 12.2 per cent).

Name of the Compound	Formula	Method of preparation and properties	Analysis	
			Found	Required for
o-hydroxy phenyl undecyl ketone	$C_{18}H_{28}O_2$	Nencki's reaction yield 65-70 per cent gives transient violet colouration with FeCl3. m.p. 44°. Bell and Driver *loc. cit.* give m.p. 44-45°		
p-Methoxy phenyl undecyl ketone	$C_{19}H_{30}O_2$	Methylation of the above ketone. Colourless liquid b. p. 110° at 50 mm.	C, 78.6; H, 10.3	C, 78.6; H, 10.4
o-hydroxy dodecyl benzene	$C_{18}H_{30}O$	By Clemmensen reduction of o-hydoxy phenyl undecyl ketone. Colourless liquid b.p. 175° at 30 mm.	C,82.4; H, 11.4	C, 82.4; H, 11.5
p-methoxy phenyl undecyl ketone	$C_{19}H_{30}O_2$	By Friedel and Crafts reaction with anisole and laury chloride. Yield 90 per cent. Crystallised from alcohol.m.p. 57°. Gave oxime m.p. 60°. On demythylation gave p-hydroxy phenyl undecyl ketone m.p. 72. Ralston and Bauer *loc. cit* give m.p. 71.5.	C, 78.7; H, 10.3	C, 78.6; H, 10.4
p-methoxy dodecyl benzene	$C_{19}H_{32}O$	Clemmensen reduction of the above ketone liquid b. p. 180 at 50 mm.	C, 82.6; H, 11.4	C, 82.6; H, 11.5
o-hydroxy phenyl tridecyl ketone	$C_{20}H_{32}O_2$	Nencki's reaction. Yield 75 per cent. Crystallised from dilute alcohol or benzene m.p. 55°. Gave orange violet colour with FeCl3. Ralston and Bauer give m.p. 52-55.		
o-methoxy phenyl tridecyl ketone	$C_{21}H_{34}O_2$	By methylation of the above ketone liquid b. p. 180-182 at 66 mm.	C, 79.2; H. 10.7	C, 79.3; H, 10.7
o-hydroxy tetradecyl benzene	$C_{20}H_{34}O$	Clemmensen reduction of o-hydroxy phenyl tridecyl ketone. Liquid b.p. 170 at 60 mm.	C, 82.8; H, 11.6	C, 82.8; H, 11.7

Name of the Compound	Formula	Method of preparation and properties	Analysis	
			Found	Required for
p-methoxy phenyl tridecyl ketone	$C_{21}H_{34}O_2$	Friedel and Crafts reaction with anisole and myristoyl chloride. Yield 90 per cent. Crystallised from alcohol m.p. 63. Gave a semicarbazone m.p. 71 and oxime m.p. 66°. Gave on demythylation phydroxy phenyl tridecyl ketone m.p. 77°. (78-80 according to Ralston and Bauer *loc. cit.*)	C, 79.2 ; H, 10.7	C, 79.3 ; H, 10.7
p-methoxy tetradecyl benzene	$C_{21}H_{36}O$	Clemmensen's reduction of the above ketone. Liquid b. p. 210° at 60 mm.	C, 82.7 ; H, 11.8	C, 82.9 ; H, 11.8
o-hydroxy phenyl pentadecyl ketone	$C_{22}H_{36}O_2$	Nencki's reaction of phenol. Yield 75 per cent m.p. 58. Ralston and Bauer give m.p. 54-56°.		
o-Methoxy phenyl pentadecyl ketone	$C_{23}H_{38}O_2$	By methylation of the above. Colourless liquid b.p. 190 at 30 mm., later solidified m.p. 38°	C, 79.7 ; H, 10.9	C, 79.8 , H, 11.0
o-Hydroxy hexadecyl benzene	$C_{22}H_{38}O$	By Clemmensen reduction of the corresponding hydroxy ketone. Liquid b. p. 210 at 45 mm.	C, 83.0 ; H, 11.9	C, 83.0 ; H, 11.95
p-Methoxy phenyl pentadecyl ketone	$C_{23}H_{38}O_2$	Friedel and Crafts reaction. Yield 90 per cent m.p. 70°. Kraft B. 21, 2269 give the m.p. 70.5°. Gave on demythylation phydroxyphenyl pentadecyl ketone m.p. 85°. Ralston and Bauer give m. p. 84°		
p-Methoxy hexadecyl benzene	$C_{23}H_{40}O$	Clemmensen reduction of the above ketone m.p. 54°.	C, 83.4 ; H, 12.0	C, 83.5 ; H, 12.1

We thank Professor Bhide, Head of the Chemistry Department, for his keen interest in this work.

MAHARAJA FRATAFSINH CHEMICAL LABORATORY,
SIR PARASHURAMBHAU COLLEGE, POONA

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SYNTHETICAL ANTHELMINTICS

Part IV—Synthesis of Lactones similar to Desmotroposantonin

By

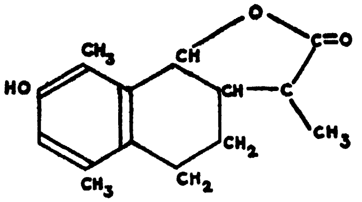
MISS K. PARANJPE, N. L. PHALNIKAR AND K. S. NARGUND

SANTONIN, the most useful anthelmintic drug, is converted by prolonged treatment with hydrochloric acid into desmotroposantonin (I) the constitution of which was established by Clemo, Haworth and Walton (J.C.S. 1930, 1110). Caius and Mhaskar (Ind. Jour. Med. Res. 1923, *11*, 371) investigated the anthelmintic properties of desmotroposantonin and concluded that it was not a good anthelmintic. This seems to contradict the conclusions of Rosenmund and Schapiro (Arch. Pharm. 1934, *272*, 313) who showed that γ-butyrolactones having a methoxy-phenyl or hydroxy-phenyl group show marked anthelmintic properties. The conclusion of Caius and Mhaskar is, however, based on the study of only one substance, *viz.*, desmotroposantonin. It was, therefore, considered desirable to study the anthelmintic properties of compounds related to desmotroposantonin and the substances prepared in this connection are described below.

The Reformatsky's reaction of ethyl bromoacetate with 1-keto-7-methoxy-1-2-3-4-tetrahydro naphthalene gave ethyl 1-hydroxy-7-methoxy 1-2-3-4-tetrahydro naphthyl-1-acetate (II). The dehydration of this with phosphorus pentoxide in benzene solution followed by alkaline hydrolysis in cold gave the unsaturated acid (III), which by treatment with cold 60 per cent sulphuric acid for 100 hours was converted into the lactone (IV). Demethylation of (IV) by hydrobromic acid in acetic acid gave the corresponding hydroxy lactone. Similar reactions have been carried out on 1-keto-5-methoxy-8-methyl-1-2-3-4-tetrahydronaphthalene and the corresponding lactones obtained. It may be mentioned that lactones described in the present paper are similar to desmotroposantonin but differ from the latter in having no methyl group in lactone ring and the position of the lactone ring itself is exactly the reverse.

EXPERIMENTAL

1-keto-7-methoxy-1-2-3-4-tetrahydro naphthalene :—It was prepared by Mitter and De's method (Jour. Ind. Chem. Soc. 1939, 35).



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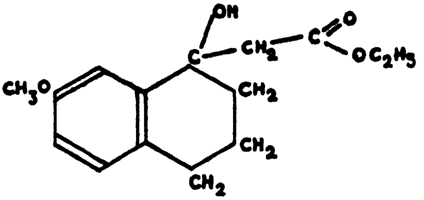

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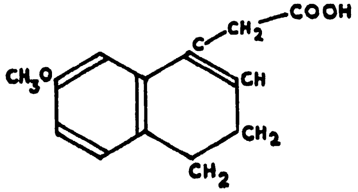
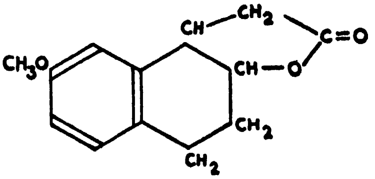


III



IV

Ethyl-1-hydroxy-7-methoxy-1-2-3-4-tetrahydro naphthyl-1-acetate :—(II) The above ketone (3.5 gms.), ethylbromoacetate (3.3 gms.), zinc shavings (1.3 gms.) and toluene (20 cc.) were heated together with a reflux condenser till a vigorous reaction set in. Heating was discontinued for some time and the reaction allowed to proceed. It was then finally refluxed for one hour to complete the reaction. It was decomposed with ice and sulphuric acid and steam-distilled to remove toluene. The residue crystallised from methyl alcohol in needles m.p. 50°. (Found : C, 68.0 ; H, 7.9 per cent ; $C_{15}H_{20}O_4$ requires C, 68.2 ; H, 7.6 per cent.)

1-hydroxy-7-methoxy-1-2-3-4-tetrahydro naphthyl 1-acetic acid :—It was obtained by cold alkaline hydrolysis of the above ester. It crystallised from dilute alcohol in needles m.p. 127°. (Found : C, 66.1 ; H, 6.8 per cent.; Eq. wt. 236.2; $C_{13}H_{16}O_4$ requires C, 66.1 ; H, 6.8 per cent; Eq. wt. 236).

Ethyl-7-methoxy3-4-dihydro-naphthyl-1-acetate :—Ethyl-1-hydroxy-7-methoxy-1-2-3-4-tetrahydro naphthyl-1-acetate (5.2 gms.) phosphorus pentoxide (5.5 gms.) and benzene (50 cc.) were heated together on water bath for four hours. Benzene was then removed, decomposed with ice, extracted with ether, dried over calcium chloride and ether removed. The residue was not purified but directly used for hydrolysis.

7-methoxy-3-4-dihydro naphthyl-1-acetic acid :—(III) It was obtained by the cold alkaline hydrolysis of the above ester. It crystallised from benzene m.p. 141.5. (Found: C, 71.6°; H, 6.5 per cent.; Eq. wt., 218.0; $C_{13}H_{14}O_3$ requires C, 71.6; H, 6.4 per cent; Eq. wt. 218.0).

Lactone of 7-methoxy-2-hydroxy-1-2-3-4-tetrahydro naphthyl-1-acetic acid :—(IV) A mixture of the acid (1 gm.) and 60 per cent sulphuric acid (20 cc.) was left at room temperature for 100 hours. It was then poured into water, extracted with ether, washed with a dilute solution of sodium bicarbonate, dried and ether removed. The residue was purified by recrystallisation from benzene, m.p. 60°. (Found : C, 71.7 ; H, 6.5 per cent; Eq. wt. by back titration, 218.9; $C_{13}H_{14}O_3$ requires C, 71.6 ; H, 6.4 per cent; Eq. wt. 218).

Lactone of 2 : 7-dihydroxy-1-2-3-4-tetrahydro naphthyl-1-acetic acid :—It was obtained by demethylating the above lactone by hydrobromic acid in acetid acid solution in the usual way. It was a colourless liquid b.p. 240° at 10 mm. (Found : C, 70.5 ; H, 5.8 per cent; Eq. wt. by back titration, 204.8. $C_{12}H_{12}O_3$ requires C, 70.5 ; H, 5.9 per cent; Eq. wt. 204.)

1-keto-5-methoxy-8-methyl-1-2-3-4-tetrahydro naphthalene :—It was obtained by boiling γ—2-methoxy-5-methyl-phenyl butyric acid with phosphorus pentoxide in benzene solution. It had b.p. 195° at 50 mm. (Found : C, 75.7; H. 7.4 per cent; $C_{12}H_{14}O_2$ requires C, 75.8 ; H, 7.4 per cent.)

Ethyl-1-hydroxy-5-methoxy-8-methyl-1-2-3-4-tetrahydro naphthyl-1-acetate :—It was prepared by Reformatsky's reaction with the above ketone in the usual way. It could not be distilled without decomposition even at reduced pressure. So it was used for hydrolysis and dehydration directly without purification.

1-hydroxy-5-methoxy-8-methyl-1-2-3-4-tetrahydro naphthyl-1-acetic acid :—It was obtained by alkaline hydrolysis of the above hydroxy ester and purified by recrystallisation from dilute acetone m.p. 90°. (Found : C, 67.2; H, 7.2 per cent; Eq. wt., 248.9; $C_{14}H_{18}O_4$ requires C, 67.2; H, 7.2 per cent ; Eq. wt., 250).

5-methoxy-8-methyl-3-4-dihydro naphthyl-1-acetic acid :—It was obtained by cold alkaline hydrolysis of the unsaturated ester obtained by dehydrating the above hydroxy ester with phosphorus pentoxide. It was a colourless liquid b.p. 192 at 50 mm. (Found : C, 72.4 ; H, 6.9; Eq. wt. 231.8; $C_{14}H_{16}O_3$ requires C, 72.4 ; H, 6.9 per cent ; Eq. wt., 232).

Lactone of 2-hydroxy-5-methoxy-8-methyl-1-2-3-4-tetrahydro naphthyl-1-acetic acid :—It was obtained by the action of cold 60 per cent; sulphuric acid on the above unsaturated acid b.p. 190 at 20 mm. (Found: C, 72.3 ; H, 6.9 per cent; Eq. wt. 231; $C_{14}H_{16}O_3$ requires C, 72.4 ; H, 6.9 per cent; Eq. wt. 232).

Lactone of 2-5-dihydroxy-8-methyl-1-2-3-4-tetrahydro naphthyl-1-acetic acid :— It was obtained by demethylating the above lactone by hydrobromic acid in acetic acid. It was liquid b.p. 180 at 40 mm. (Found : C, 71.6 ; H, 6.4 per cent; Eq. wt. by back titration, 218.7; $C_{13}H_{14}O_3$ requires C, 71.5 ; H, 6.4 per cent; Eq. wt. 218).

We thank Professor Bhide, Head of the Chemistry Department, for his keen interest in this work.

MAHARAJA PRATAPSINHA CHEMICAL LABORATORY,
SIR PARASHURAMBHAU COLLEGE, POONA

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SYNTHETICAL ANTHELMINTICS

Part V—γ-p-alkoxyphenyl butyrolactones

By

J. J. TRIVEDI AND K. S. NARGUND

ROSENMUND and Schapiro (Arch. Pharm. 1934, *272*, 313), showed that γ-p-methoxy-phenyl butyrolactone had thrice the anthelmintic properties of santonin. It is therefore evident that a free phenolic group is not necessary. This is also evident from the fact that anethol and safrol are excellent vermicides. The presence of an alkyl group endows phenols with valuable properties so that they could be used as internal antiseptics. It is not necessary that the alkyl group should be present as substituent in the nucleus It may be present as part of an ether. Thus it has been shown that the bactericidal properties of resorcinol compounds with alkyl substituents is practically the same with the substituent radical in the nucleus or attached to one oxygen atom as an ether (J.A.C.S. 1931, 3397). It was therefore decided to study the anthelmintic properties of γ-alkoxy-phenyl butyrolactones. The present paper gives compounds up to γ-p-hexyloxy-phenyl-butyrolactone.

β-p-alkoxy-benzoyl-propionic acids were prepared by the Friedel and Craft's reaction of an appropriate phenol ether with succinic anhydride in nitrobenzene as solvent. The constitution of these compounds is evident from the fact that identical compounds were obtained by the action of an appropriate alkyl bromide in presence of potassium carbonate in acetone solution on ethyl β-p-hydroxy benzoyl propionate of Raval, Bokil and Nargund (Jour. Bom. Univ. 1938, *7*, 3, 184). Reduction of these βp alkoxy benzoyl propionic acids by sodium and alcohol and the conversion of the resulting hydroxy acids into lactones was carried out as described by Trivedi and Nargund (Jour. Bom. Univ. 1941, *10* 3, 99).

EXPERIMENTAL

Phenetol, n propoxy, isopropoxy, n butoxy, isobutoxy, isoamyloxy and n hexyloxy benzenes were prepared by the action of an appropriate alkyl bromide on phenol in presence of sodium ethoxide, n hexyloxy benzene does not seem to have been described before. It had b.p. 240 at 760 mm. $D_4^{38^\circ} = 0.90083$ and $N_D^{38} = 1.4779$. (Found : C, 80.7; H, 10.3 per cent. $C_{12}H_{18}O$ requires C, 80.9; H, 10.1 per cent).

General procedure for Friedel and Craft's condensation :—To a well cooled mixture of alkoxybenzene (0.1 mol.) succinic anhydride (0.1 mol.) and nitrobenzene (75 gms.) was added anhydrous aluminum chloride (28 gms.) in three lots with good shaking. It was then left at room temperature for four hours. It was then decomposed with ice and hydrochloric acid and steam distilled to remove nitrobenzene. The resulting solid was purified by dissolving in a solution of sodium carbonate, filtering and reprecipitating with an acid. The yields of keto acids were good in all the cases (80-90 per cent). Isopropoxy benzene did not condense with succinic anhydride by the above procedure.

Preparation of the above keto acids by a different method which proves their constitutions. Ethyl βp hydroxybenzoylpropionate (3 gms.), anhydrous potassium carbonate (3 gms.), alkyl bromide (3 gms.) and acetone (15 cc.) were heated together on water bath for 12 hours. Acetone was removed and the pasty residue was hydrolysed by boiling with excess of a solution of sodium hydroxide. The product was recovered by acidification. The keto acids obtained by this procedure were identical with the corresponding acids obtained in Friedel and Craft's reaction.

The m.p. of keto acids recorded in the table are temperatures at which a clear liquid was formed. Four or five degrees below these temperatures the keto acids gave turbid liquids probably due to liquid crystals. A similar phenomenon has been observed by Jones in case of p alkoxy benzoic acids (J.C.S. 1934, 1874). The compounds are described in a tabular form for the sake of brevity.

Name of the Compound	Formula	Properties	Analysis	
			Found	Required for
β-p ethoxy benzoyl propionic acid	$C_{12}H_{14}O_4$	Soluble. in alcohol, acetic acid, ethylacetate and chloroform, insoluble in petrol. Prismatic needles from benzene or water m.p. 137-138°	C, 64.6 : H, 6.4 Eq. wt. 221.6	C, 64.9; H, 6.3 Eq. wt. 222
Semicarbazone of the above	$C_{13}H_{17}O_4N_3$	Prepared in the usual manner m.p. 189°	Eq. wt. 281.4	Eq. wt. 279
Ethyl β-p-ethoxybenzoyl propionate	$C_{14}H_{18}O_4$	Long needles from chloroform m.p. 52°	C, 67.2; H, 7.4	C, 67.2; H, 7.2
Methyl β-p-ethoxybenzoyl propionate	$C_{13}H_{16}O_4$	Needles from chloroform. m.p. 50-51°	C, 65.9, H. 6.9	C, 66.1; H, 6.8
γ-p-ethoxy phenyl butyrolactone	$C_{12}H_{14}O_3$	Flat needles or plates from alcohol m.p. 73-74°	C, 69.6; H, 6.8 Eq. wt. 206.3	C, 69.9; H, 6.8 Eq. wt. 206
β-n-propoxybenzoyl propionic acid	$C_{13}H_{16}O_4$	Long thin needles from hot water or dilute alcohol m.p. 118-119°	C, 66.0; H, 6.6 Eq. wt. 233.4	C, 66.1; H, 6.8 Eq. wt. 236
Semicarbazone of the above	$C_{14}H_{19}O_4N_3$	Crystallised from alcohol m.p. 178-179°	Eq. wt. 291.3	Eq. wt. 293
Methyl β-p-n propoxybenzoyl propionate	$C_{14}H_{18}O_4$	Needles from petrol m.p. 58°	C, 66.9, H, 7.5	C. 67.2; H, 7.2
γ-n-propoxyphenyl butyrolactone	$C_{13}H_{16}O_3$	Flakes from petrol m.p. 64°	C, 70.9: H, 7.5 Eq. wt. 216.1	C, 70.9; H, 7.3 Eq. wt. 220
γ-hydroxy-γ-n-propoxyphenyl butyric acid	$C_{13}H_{18}O_4$	Needles from benzene m.p. 101	C, 65.4; H, 7.5 Eq wt 234.9	C, 65.5; H, 7.6 Eq. wt. 238
β-p-n-butoxy benzoyl propionic acid	$C_{14}H_{18}O_4$	Long thin needles from dilute alcohol m.p. 112°	C, 67.4; H. 7.5 Eq. wt. 251.3	C, 67.2; H, 7.2 Eq. wt. 250
Semicarbazone of the above	$C_{15}H_{21}O_4N_3$	m.p. 171-172°	Eq. wt. 305.0	Eq. wt. 307
Methyl-β-p- n butoxybenzoyl propionate	$C_{15}H_{20}O_4$	Long needles from dilute methyl alcohol m.p. 43-44°	C, 68.1; H, 7.9	C, 68.2; H, 7.6
Ethyl-β-p-n butoxybenzoyl propionate	$C_{16}H_{22}O_4$	Liquid b.p. 240° at 20mm. $D_4 37.2=1.064$ $N_D 37.2=1.5090$	C, 69 3: H, 7.8	C, 69.1; H, 7.9
γ-p-n-butoxyphenyl butyrolactone	$C_{14}H_{18}O_3$	Flakes or plates from petrol m.p. 63-64	C, 71.7: H, 7 9 Eq. wt. 233.1	C, 71.8; H, 7.7 Eq. wt. 234
γ-hydroxy-γ-p-n-butoxyphenyl butyric acid	$C_{14}H_{20}O_4$	Flat needles from benzene petrol mixture m.p. 80°	C, 66.6, H, 8.1 Eq. wt. 259	C, 66.7, H, 7.9 Eq. wt. 252
β-p-isobutoxybenzoyl propionic acid	$C_{14}H_{18}O_4$	Plates from dilute methyl alcohol m.p. 131-132°	C, 67.1; H, 7.5 Eq. wt. 246.9	C, 67.2; H, 7.2 Eq. wt. 250
Semicarbazone of the above	$C_{15}H_{21}O_4N_3$	m.p. 188-189°	Eq. wt. 305	Eq. wt. 307

Name of the Compound	Formula	Properties	Analysis	
			Found	Required for
γ-p-isobutoxyphenyl butyrolactone	$C_{14}H_{18}O_3$	Colourless liquid b p. 198° at 5 mm. $D_4 35.5=1.0849$ $N_D 35.5=1.5166$	C, 71.5 ; H, 7.9 Eq. wt. 230.1	C, 71.8 ; H, 7.7 Eq. wt. 234
γ-hydroxy-γ-p-isobutoxy phenyl butyric acid	$C_{14}H_{20}O_4$	Needles from benzene petrol mixture m.p. 73°	Eq. wt. 255.1	Eq. wt. 252
β-p-isoamyloxybenzoyl propionic acid	$C_{15}H_{20}O_4$	Short thin needles from dilute alcohol m.p. 120°	C, 68.0 ; H, 7 8 Eq. wt. 266	C, 68.2 ; H, 7.6 Eq. wt. 264
Semicarbazone of the above	$C_{16}H_{23}O_4N_3$	m p. 185°	Eq. wt. 314.5	Eq. wt. 321
γ-p-isoamyloxy phenyl butyrolactone	$C_{15}H_{20}O_3$	Sq. plates from ethyl alcohol m.p. 74°	C, 72.5 ; H, 8.4	C, 72.6 ; H, 8.1
γ-hydroxy-γ-p isoamyloxyphenyl butyric acid	$C_{15}H_{22}O_4$	Flat needles from benzene petrol mixture m.p. 83-84°	Eq. wt. 270	Eq. wt. 266
β-p-hexyloxybenzoyl propionic acid	$C_{16}H_{22}O_4$	Silky needles from dilute alcohol m.p. 109°	C, 69.3 ; H, 7.9 Eq. wt. 283	C, 69.1 ; H, 7.9 Eq. wt. 278
Semicarbazone of the above	$C_{17}H_{25}O_4N_3$	Cubes from alcohol m.p. 181°	Eq. wt. 330.5	Eq. wt. 335
γ-p-hexyloxy phenyl butyrolactone	$C_{16}H_{22}O_3$	Plates from dilute alcohol m.p. 66-67°	C, 73.0 ; H, 8.5	C, 73.3 ; H, 8.4

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M. R. SCIENCE INSTITUTE,
GUJARAT COLLEGE, AHMEDABAD

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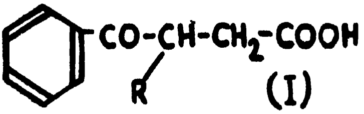
CONDENSATION OF METHYL SUCCINIC ANHYDRIDE

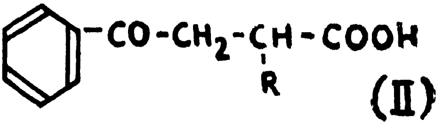
With Cresol Methyl Ethers

By

B. L. Bhatt and K. S. Nargund

THE condensation of an unsymmetrically substituted succinic anhydride by Friedel and Craft's reaction is likely to yield two different keto acids as shown below :—


(I)


(II)

Methyl-succinic anhydride was condensed with benzene by Meyer and Stamm (B. 1923, *56*, 1424) who isolated both the above types of keto acids. Robinson and Waters (J.C.S. 1933, 83) condensed methyl-succinic anhydride with veratrole while Mitter and De (Jour. Ind. Chem. Soc. 1939, 199) condensed it with anisole, rescorinol dimethyl ether and pyrogallol trimethyl ether. In all these cases the main product was a keto acid of type II, the isomeric keto acid of type I being formed in small quantities in some cases. We have condensed methyl succinic anhydride with cresol methyl ethers using different solvents such as nitrobenzene, carbondisulphide and acetylene tetrachloride and found that only one type of keto acids was formed, *viz.*, type II. The use of nitrobenzene gave a maximum yield of the keto acid. The same keto acids were formed when carbondisulphide or acetylene tetrachloride were used as solvent but in much poorer yield and impure condition.

The condensation of methyl succinic anhydride with o-cresol methyl ether gave a keto acid m.p. 124°. On oxidation with sodium hypobromite it gave 4-methoxy-3-toluic acid. It reacted with salicyl aldehyde in presence of dry hydrogen chloride at low temperature to give a deep red pyrylium derivative thus indicating the presence of $-COCH_2$ grouping (Decker and Fallenberg. Ann, 1907, *356*, 302; Perkin, Robinson and Turner, J.C.S. 1908, 1085). Therefore the constitution of the keto acid was α methyl β-4-methoxy-3-toluoyl propionic acid, m-cresol-methyl ether and methyl succinic anhydride gave a keto acid m.p. 113° which on oxidation gave 4-methoxy-2-toluic acid. It also gave a pyrylium derivative. Hence its constitution was α methyl-B-4-methoxy-2-toluoyl propionic acid. p-cresol methyl ether and methyl succinic anhydride gave a keto acid m.p. 129° which formed a pyrylium derivative and on oxidation gave 2-methoxy-5-toluic acid. Hence its constitution was α methyl-β-2-methoxy-5-toluoyl propionic acid.

All the above keto acids have been characterised by suitable derivatives such as methyl and ethyl esters and semicarbazones.

EXPERIMENTAL

General procedure for Friedel and Craft's reaction :—Methyl succinic anhydride (0.1 mol.), cresol methyl ether (0.1 mol.), nitrobenzene (75 gms.) and anhydrous aluminum chloride (28 gms.) were mixed together in cold and kept at room temperature for four hours. It was then decomposed with ice and hydrochloric acid and steam distilled to remove nitrobenzene. The solid residue thus obtained was purified by sodium carbonate treatment. The yields obtained are given in the following table.

Phenol Ether Used	Product Obtained	Per Cent Yield of the Pure Crystallised Product
o-cresol methyl ether ..	α methyl β4-methoxy-3-toluoyl propionic acid	40 per cent
m-cresol methyl ether ..	α methyl β4-methoxy-2-toluoyl propionic acid	20 per cent
p-cresol methyl ether ..	α methyl β2-methoxy-5-toluoyl propionic acid	33 per cent

α *Methyl-β-4-methoxy-3-toluoyl propionic acid* :—It was soluble in ethyl and methyl alcohol, benzene, chloroform and hot acetic acid from which it crystallised in prisms m.p. 124°. It formed an insoluble silver salt. Barium and lead salts were soluble in hot water. (Found : C, 65.8 ; H, 7.0 per cent. Eq. wt., 238.0. Ag. in silver salt, 31.82 per cent. $C_{13}H_{16}O_4$ requires C, 66.1 ; H, 6.8 per cent. Eq. wt. 236.0. $C_{13}H_{15}O_4$ Ag. requires Ag. 31.49 per cent). On oxidation it gave an acid m.p. 192 identified as 4-methoxy-3-toluic acid. Semicarbazone of the above acid formed in the usual manner had m.p. 170° with decomposition. (Found: Eq. wt. 289.2. $C_{14}H_{19}O_4N_3$ requires Eq. wt. 293).—*Methyl α methyl β4-methoxy-3-toluoyl propionate* perpared by Fischer Speier method was a colourless liquid b.p. 190-192° at 13mm. and had $N_D^{36} = 1.5269$ and $D_4^{36} = 1.116$. (Found: C, 67.1 ; H, 7.5 per cent. $C_{14}H_{18}O_4$ requires C, 67.2 ; H, 7.2 per cent). *Ethyl α methyl β4-methoxy-3-toluoyl propionate* prepared similarly had b.p. 197-198° at 10 mm. $N_D^{36} = 1.5191$

and D_4^{36} =1.0906. (Found : C, 68.0 ; H, 7.9 per cent. $C_{15}H_{20}O_4$ requires C, 68.2 ; H, 7.6 per cent).

α methyl β 4-methoxy-2-toluoyl propionic acid :—It was soluble in methyl and ethyl alcohol, ethyl acetate, chloroform, and hot benzene. It was crystallised from acetic acid in granules m.p. 113°. Silver and lead salts were insoluble while barium and calcium salts were soluble in water. (Found: C, 65.9; H, 7.0 per cent. Eq. wt. 234.8. $C_{13}H_{16}O_4$ requires C, 66.1 ; H, 6.8 per cent. Eq. wt. 236.0). Semicarbazone of the above prepared in the usual manner had m.p. 172-173°. (Found : Eq. wt. 294.0. $C_{14}H_{19}O_4N_3$ requires Eq. wt. 293). *Methyl α methylB4-methoxy-2-toluoyl propionate* was a colourless liquid b.p. 187-189 at 12 mm. and had N_D^{30} =1.5248. (Found : C, 67.0 ; H, 7.3 per cent. $C_{14}H_{18}O_4$ requires C, 67.2 ; H, 7.2 per cent). *Ethyl α methyl β 4-methoxy-2-toluoyl propionate* had b.p. 193° at 11 mm. N_D^{30} =1.5184. (Found : C, 68.1 ; H, 7.6 per cent. $C_{15}H_{20}O_4$ requires C, 68.2 ; H, 7.6 per cent).

α-methyl-β-2-methoxy-5-toluoyl propionic acid :—It was soluble in alcohol, acetic acid, chloroform, ethyl acetate and hot benzene. Crystallised in needles from benzene m.p. 129°. Silver and leads salts were insoluble while barium and calcium salts were soluble in water. (Found : C, 66.2; H, 7.0 per cent. Eq. wt. 234.8 $C_{13}H_{16}O_4$ requires C, 66.1 ; H, 6.8 per cent. Eq. wt. 236). On oxidation it gave 2-methoxy-5-toluic acid m.p. 68°. The keto acid did not form a semicarbazone under the usual condition. *Methyl α methyl β-2-methoxy-5-toluoyl propionate* was a colourless liquid b.p. 176°-180° at 9 mm. and had D_4^{35} =1.104 and N_D^{35}= 1.5125. (Found : C, 67.3 ; H, 7.4 per cent. $C_{14}H_{18}O_4$ requires C, 67.2 ; H, 7.2 per cent). *Ethyl α methyl-β-2-methoxy-5-toluoyl propionate* was a liquid b.p. 160° at 3 mm. and had D_4^{35} =1.075 and N_D^{35} = 1.5051. (Found : C, 68.3 ; H, 7.7 per cent. $C_{15}H_{20}O_4$ requires C, 68.2 ; H, 7.6).

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M. R. Science Institute,
Gujarat College, Ahmedabad

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ALKYL SUCCINIC ACIDS

Part II—n-Amyl and n-Decyl Succinic Acids

By

S. U. MEHTA AND K. S. NARGUND

THE purpose of preparing alkyl succinic acids as well as the best mode of their preparation have been described before (Mehta and Nargund, Jour. Bom. Univ. 1942, vol. *10*, part 5, 141). Following the same methods we have now prepared the substituted succinic acids named in the title of this paper.

n-Amyl succinic acid has been previously reported to be a liquid b.p. 200 at 20 mm. It was obtained by the decomposition of *γhexylidene-γ-hexyl-γ-butyrolactone* (E. Bl. 4, 5, 1143, Chem. Zentr. 1910, i, 514). As all the lower alkyl succinic acids are well defined solids it seemed to us unlikely that n-amyl succinic acid should be a liquid. We have now prepared n-amyl succinic acid by the malonic ester synthesis from ethyl α bromo heptoate. n-Amyl succinic acid is now found to be a solid m.p. 81-82°. It has been characterised by a number of derivatives. n-Decyl succinic acid has been similarly prepared from ethyl-α bromo laurate.

EXPERIMENTAL

Heptoic acid and lauric acid were brominated by Hell volhard method and converted into ethyl esters by treatment with absolute alcohol. The other reactions were carried out as described previously and compounds described in tabular form.

Name of the Compound	Formula	Properties	Analysis	
			Found	Required for
n-heptane 1-1-2-tricarboxylic acid	$C_{10}H_{16}O_6$	Very soluble in hot water. Sol. in ethyl acetate, acetic acid and benzene, Insol. in petrol. Small flat needles from acetic acid m.p. 134-135°	C, 51.5; H, 7.1 Eq. wt. 77.0	C, 51.7; H, 6.9 Eq. wt. 77.3
n-Amyl succinic acid	$C_9H_{16}O_4$	Prepared by heating the above to 190°. Sol. in benzene, water, acetic acid and hot petrol. Crystallised in granules from petrol m.p 81-82°	C, 57.2; H, 8.8 Eq. wt. 95.0	C, 57.4; H, 8.5 Eq. wt. 94.0
n-Amyl succinic anhydride	$C_9H_{14}O_3$	Prepared from the above acid and acetyl chloride. Colourless liquid b.p. 140 at at 13 mm.	C, 63.7; H, 8.5	C, 63.6; H, 8.2
Semianilide of n-amyl succinic acid	$C_{15}H_{21}O_3N$	Prepared from anhydride and the requisite quantity of aniline. Thin plates from benzene m.p. 112-115°	Eq. wt. 260.0	Eq. wt. 263
Semi-p-Toluidide of n-amyl succinic acid	$C_{16}H_{23}O_3N$	Preparedsimilarly to anilide. Needles from benzene m.p. 122-124°	Eq. wt. 272.6	Eq. wt. 277.0
n-dodecane-1-1-2-tricarboxylic acid	$C_{15}H_{26}O_6$	Sol. in alcohol, hot chloroform, hot ethyl acetate and acetic acid. Insol in water, and petrol. Short needles from acetic acid m.p. 135°	C, 59.4; H, 8.8 Eq. wt. 98.5	C, 59.6; H, 8.6 Eq. wt. 100.0
n-Decyl succinic acid	$C_{14}H_{26}O_4$	Obtained by heating the above. Sol. in alcohol, ethyl acetate, chloroform and acetic acid. Crystallised in plates from dilute acetic acid m.p. 94-95°	C, 65.3; H, 10.3 Eq. wt. 127.0	C, 65.1; H, 10.1 Eq. wt. 129
n-Decyl succinic anhydride	$C_{14}H_{24}O_3$	Prepared by the action of acetyl chloride on the above. Fine long needles from petrol m.p. 70-71°	C, 69.8; H, 10.4	C, 70.0; H, 10.0
Semi anilide of n-decyl succinic acid	$C_{20}H_{31}O_3N$	Prepared from anhydride and the requisite quantity of aniline. Needles from alcohol m.p. 103-104°	Eq. wt. 330.1	Eq. wt. 333.0
Ethyl n-decyl succinate	$C_{18}H_{34}O_4$	From the acid and alcohol by Fischer. Speier method. Colourless liquid b.p. 175-180 at 13 mm. $D^{33\cdot6}_{4}=0.9124$ and $N^{33\cdot6}_{D}=1.4342$	C, 68.7; H. 10.9	C, 68.8; H, 10.8

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M. R. SCIENCE INSTITUTE,
GUJARAT COLLEGE, AHMEDABAD

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TRANSFORMATION OF O-NITROBENZOYLOXYACETOARONES TO O-HYDROXYNITROBENZOYLAROYLMETHANES

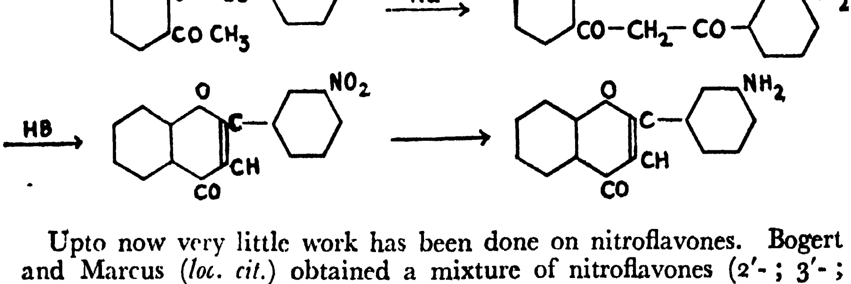
And the Synthesis of Nitroflavones

By

V. V. VIRKAR

IN continuation of the previous work by Virkar and Wheeler (J.C.S., 1939, 1679) on the transformation, by the action of metallic sodium of *o*-benzoyloxy or *o*-naphthoyloxy acetoarones to corresponding *o*-hydroxydiaroylmethanes and the cyclisation of the latter to chromones with hydrogen bromide in acetic acid, it has now been observed that nitrobenzoyloxyacetoarones also undergo similar molecular rearrangement with metallic sodium, giving corresponding *o*-hydroxynitrobenzoylaroylmethanes, which finally give nitroflavones. These nitroflavones further formed aminoflavones on reduction.

o-(3′-Nitrobenzoyloxy) acetophenone on treatment with metallic sodium formed 2-hydroxy-3-′nitrobenzoylmethane, which further formed 3′-nitroflavone on dehydration. The 3′-nitroflavone was reduced to 3′-aminoflavone by the method followed by Bogert and Marcus (J.Am. Chem. Soc. 1919, *41*, 83).



Upto now very little work has been done on nitroflavones. Bogert and Marcus (*loc. cit.*) obtained a mixture of nitroflavones (2′- ; 3′- ; 4′-nitro) by nitrating a flavone with nitric acid, which they could not separate due to the similarity of all the nitroflavones with regard to the solubility in the solvents tried. Moreover all their attempts to limit the action of nitric acid to the formation of only one nitroflavone failed. However the corresponding aminoflavones (2′- ; 3′- ; 4′-amino) obtained by reduction were separated without much difficulty. But by the transformation method all the nitroflavones can be formed separately without any difficulty.

Similarly 1-(3'-nitrobenzoyloxy)-2-acetonaphthone and 1-(4'-nitrobenzoyloxy)-2-acetonaphthone with metallic sodium gave 1-hydroxy-3'-nitrobenzoyl-2-naphthoylmethane and 1-hydroxy-4'-nitrobenzoyl-2-naphthoylmethane respectively. These on cyclisation formed 3'- and 4'-nitro-7 : 8-benzoflavones, which were further reduced to corresponding aminoflavones.

When 2-benzoyloxy-4-methoxy-5-nitroacetophenone was treated with metallic sodium, no reaction took place and the substance remained unchanged. Ullal, Shah and Wheeler (J. Univ. Bom., 1941, *10*, part 3, 118) also stated that no migration of *o*-aroyloxy group occurred with sodium ethoxide in the *o*-aroyloxy derivative of a nitroacetophenone, but hydrolysis was mainly observed. This behaviour may be due to the presence of a negative group (NO_2) in the ketonic portion of a compound, thus inhibiting the migration of the *o*-aroyloxy group.

EXPERIMENTAL

Preparation of o-*nitrobenzoyloxyacetoarones.*

o-(3'-Nitrobenzoyloxy)acetophenone (10 g.) was prepared by heating a mixture of *o*-hydroxyacetophenone (6.8 g.), m-nitrobenzoylchloride (9.2 g.) and pyridine (20 cc.) at 100°*C.*; crystallised from alcohol in white shining needles with m.p. 99-100°*C.* (Found : N, 5.0 per cent ; $C_{15}H_{11}O_5N$ requires N, 4.9 per cent).

Similarly were prepared, 1-(3'nitrobenzoyloxy)2--acetonaphthone (14.0 g.) from 1-hydroxy-2-acetonaphthone (10.0 g.), m-nitrobenzoylchloride (10.0 g.) and pyridine (30 cc.), crystallised from glacial acetic acid in colourless small needles with m.p. 152°*C.* (Found : N, 4.3 per cent ; $C_{19}H_{13}O_5N$ requires N, 4.2 per cent) ; and 1-(4'-nitrobenzoyloxy)-2-acetonaphthone (7.25 g.) from 1-hydroxy-2-acetonaphthone (5.0 g.), p-nitrobenzoylchloride (5.0 g.) and pyridine (15.0 cc.), crystallised from glacial acetic acid as a colourless microcrystalline solid with m.p. 151°*C.* (Found : N, 4.3 per cent ; $C_{19}H_{13}O_5N$ requires N, 4.2 per cent).

Rearrangement of o-*nitrobenzoyloxyacetoarones to* o-*hydroxynitrobenzoylaroylmethanes and cyclisation to nitrochromones.*

3'-Nitroflavone :—

A mixture of *o*-(3'-nitrobenzoyloxy)acetophenone (2.8 g.), pulverised sodium (0.3 g.) and dry toluene (10.0 cc.) was heated at 130°*C* for two hours and the separated yellow sodium salt of 2-hydroxy-3'-nitrodibenzoylmethane was collected and was first treated with alcohol to dissolve any residual excess of sodium and then acidified with dilute hydrochloric acid. 2-Hydroxy-3'-nitrobenzoylmethane (1.5 g.) separated was crystallised from alcohol or glacial acetic acid in yellow crystals with m.p. 157°*C.* (Found : N, 4.9 per cent ; $C_{15}H_{11}O_5N$ requires N, 4.9 per cent). This substance (1.5 g.) was dissolved in glacial acetic acid (8.0 cc.) and to the warm solution hydrogen bromide in acetic acid (10 cc.) was added and the reaction mixture was allowed to remain for fifteen minutes. 3'-Nitroflavone (1.2 g.) which separated on dilution with water, crystallised from glacial acetic acid in white shining small needles with m.p. 203°*C*. (Found : C, 67.5 per cent ; H, 4.2 per cent and N, 5.2 per cent ; $C_{15}H_9O_4N$ requires C, 67.4 per cent ; H, 4.2 per cent and N, 5.2 per cent).

3'-Aminoflavone :—

To a hot mixture of 3'-nitroflavone (0.2 g.) and absolute alcohol (10.0 cc.), strannous chloride (5.0 cc.), concentrated hydrochloric acid (10.0 cc.) and metallic tin (about 0.1 g.) were added and the whole mixture was heated under reflux for half an hour during which time it formed a clear yellow solution. The reaction mixture was then further heated for about fifteen minutes. It was diluted with water and tin was removed as stannous sulphide by passing hydrogen sulphide gas. The solution obtained after removing hydrogen sulphide was concentrated and treated with solid sodium carbonate to precipitate 3'-aminoflavone. 3'-Aminoflavone thus obtained was crystallised by dissolving in hot pyridine and keeping at 0°*C*, in yellow thin shining plates with m.p. 155 *C*. (Found : N, 5.8 per cent ; $C_{15}H_{11}O_2$ N requires N, 5.9 per cent).

Bogert and Marcus (*loc. cit.*) isolated it from the mixture of 2'-, 3'- and 4'-aminoflavones and give the m.p. 156-157°*C*.

3'-Nitro-7 : 8-benzoflavone :—

A mixture of 1(3'-nitrobenzoyloxy)-2-acetonaphthone (5.0 g.) pulverised sodium (1.2 g.) and dry toluene (20 cc.) was heated at 130°*C* for two hours. The separated yellow sodium salt of 1-hydroxy-3'-nitrobenzoyl-2-naphthoylmethane was collected and first treated with alcohol to dissolve any residual excess of sodium and then acidified with dilute hydrochloric acid. 1-Hydroxy-3'-nitrobenzoyl-2-naphthoylmethane (4.0 g.) separated was crystallised from excess of acetone in brown small shining plates with m.p. 196°*C*. (Found : N, 4.2 per cent ; $C_{19}H_{13}O_5N$ requires N, 4.2 per cent). The hot solution of this substance (1.5 g.) in glacial actic acid (20 g.) was treated with hydrogen bromide in acetic acid (20 cc.) and was kept for about twenty-four hours. 3'-Nitro-7 : 8-benzoflavone (1.1 g.) which separated on dilution with water, crystallised from glacial acetic acid and had m.p. 262°*C*· (Found : C, 71.9 per cent ; H, 3.5 per cent ; N, 4.3 per cent ; $C_{19}H_{11}O_4N$ requires C, 71.9 per cent ; H, 3.5 per cent ; and N .4.4 per cent).

3'-Amino-7 : 8-benzoflavone :—

To a mixture of 3'-nitro-7 : 8-benzoflavone (0.5 g.) and glacial acetic acid (30 cc.), stannous chloride (15 cc.), metallic tin (0.5 g.) and concentrated hydrochloric acid (15 cc.) were added and the whole reaction mixture was heated under reflux for about one and half hour, during which time it formed a clear yellow solution. It was then kept in frigidaire overnight and the hydrochloride separated in yellow crystalline state was filtered off and washed with glacial acetic acid. The m.p. of the hydrochloride was above 300°*C*.

The hydrochloride on treatment with water formed a solution from which 3'-amino-7 : 8-benzoflavone was precipitated by treating the solution with solid sodium carbonate. The compound could not be crystallised from most of the organic solvents and so it was redissolved in dilute hydrochloric acid, filtered and precipitated by sodium carbonate solution. It separated as a yellow powder with m.p. above 300°*C.* (Found : N, 4.8 per cent ; $C_{19}H_{13}O_2N$ requires N, 4.9 per cent).

4'-Nitro-7 : 8-benzoflavone :—

Similarly 1-hydroxy-4'-nitrobenzoyl-2-naphthoylmethane (4.0 g.) was obtained from 1-(4'-nitrobenzoyloxy)2-acetonaphthone (5 g.) after sodium (1.2 g.) treatment. It crystallised from acetone in orange crystals with m.p. 222°*C.* (Found : N, 4.4 per cent ; $C_{19}H_{13}O_5N$ requires N, 4.2 per cent). A mixture of this substance (1.0 g.), glacial acetic acid (15 cc.) and hydrogen bromide in acetic acid (15 cc.) was kept at room temperature for half an hour. 4'-Nitro-7 : 8-benzoflavone (quantitative yield) separated on dilution with water and crystallised from glacial acetic acid with m.p. 293°*C.* (Found : C, 71.9 per cent ; H, 3.5 per cent ; N, 4.1 per cent ; $C_{19}H_{11}O_4N$ requires C, 71.9 per cent ; H, 3.5 per cent and N, 4.4 per cent).

4'-Amino-7 : 8-benzoflavone :—

To a mixture of 4'-nitro-7 : 8-benzoflavone (0.2 g.) and glacial acetic acid (10 cc.), stannous chloride (10 cc. or excess), concentrated hydrochloric acid (10 cc.) and metallic tin (about 0.2 g.) were added and the whole reaction mixture was heated under reflux for two to three hours, during which time the yellow colour of the reaction mixture changed to reddish brown. It was then kept overnight at room temperature during which time the hydrochloride of the amino compound separated in crystalline state, the m.p. of which was higher than 300°*C.*

The hyprochloride on treatment with water formed a solution from which the amino compound was separated by treating the solution with sodium carbonate. 4'-Amino-7 : 8-benzoflavone could not be crystallised satisfactorily from most of the organic solvents. It was dissolved in pyridine, slightly diluted with water and allowed to separate by cooling the solution in frigidaire. It separated as yellow powder with m.p. 265°*C.* (Found : N, 4.8 per cent ; $C_{19}H_{13}O_2N$ requires N, 4.9 per cent).

With concentrated sulphuric acid it gave greenish yellow fluorescence, while with concentrated nitric and hydrochloric acid it gave no fluorescence.

With dilute pyridine solution it gave same type of fluorescence as with sulphuric acid. With absolute alcohol it gave green fluorescence, while with ether and chloroform it gave light and bright crimson fluorescence respectively.

DEPARTMENT OF ORGANIC CHEMISTRY,
ROYAL INSTITUTE OF SCIENCE, BOMBAY
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CHROMONES OF THE NAPHTHALENE SERIES—PART

(Transformation of *o*-naphthoyloxyacetoarones to *o*-hydroxydiaroylmethanes)

By

V. V. VIRKAR AND R. C. SHAH

IN continuation of the previous work by Virkar and Wheeler (J.C.S., 1939, 1679) on the transformation, by the action of metallic sodium, of o-aroyloxyacetoarones to o-hydroxydiaroylmethanes and the cyclisation of the latter to chromones α- and β-naphthoyloxy derivatives of o-hydroxyacetophenone and 4-benzoyloxy-2-hydroxyacetophenone were treated with metallic sodium to get the respective transformation products, from which the corresponding 2-naphthylchromones were obtained by dehydration. Thus some more 2-naphthylchromones with good yields were synthesised through the intermediate o-hydroxydiaroylmethanes.

2-Benzoyloxy-4-methoxyacetophenone was also successfully treated with metallic sodium from which 7-methoxyflavone was obtained in good yield.

EXPERIMENTAL

Preparation of o-Aroyloxyacetoarones :—

o-(α-Naphthoyloxy) acetophenone (12 g.) separated when a mixture of o-hydroxyacetophenone (6.8 g.), α-naphthoylchloride (9.5 g.) and pyridine (15 cc.), which had been heated at 100°*C* for half an hour, was poured into dilute hydrochloric acid. It was first washed with dilute sodium hydroxide and then with water ; crystallised from alcohol into colourless crystals with m.p. 108°*C*. (Found : C, 78.9 per cent ; H, 4.9 per cent ; $C_{19}H_{14}O_3$ requires C, 78.6 per cent ; H, 4.8 per cent).

Similarly o-(β-naphthoyloxy) acetophenone (10.5 g.) from o-hydroxyacetophenone (6.8 g.), β-naphthoylchloride (9.5 g.) and pyridine (15 cc.) crystallised from alcohol in white crystals with m.p. 119°*C*. (Found : C, 78.7 per cent ; H, 4.8 per cent ; $C_{19}H_{14}O_3$ requires C, 78.6 per cent and H, 4.8 per cent). 4-Benzoyloxy-2-(1′-naphthoyloxy) acetophenone (27 g.) from 4-benzoyloxy-2-hydroxyacetophenone (25 g.), α-naphthoyl chloride (18 g.) and pyridine (40 cc.)

crystallised from alcohol in white cotton like clusters of needles with m.p. 104°*C*. (Found : C, 76.3 per cent ; H, 4.4 per cent ; $C_{26}H_{18}O_5$ requires C, 76.1 per cent and H, 4.4 per cent) ; 4-Benzoyloxy-2-(2'-naphthoyloxy) acetophenone (12.5 g.) from 4-benzoyloxy-2-hydroxyacetophenone (25 g.), β-naphthoylchloride (9.5 g.) and pyridine (30 cc.) crystallised from alcohol as a white microscrystalline solid with m.p. 103-104°*C*. (Found : C, 76.3 per cent ; H, 4.4 per cent ; $C_{26}H_{18}O_5$ requires C, 76.1 per cent and H, 4.4 per cent) ; and 4-Methoxy-2-benezoyloxyacetophenone (Benzoyl pæonol) (12.5 g.) separated in a pasty form, from 4-methoxy-2-hydroxyacetophenone (10 g.) benzoylchloride (9.4 g.) and pyridine (12 cc.). It was extracted with ether from its reaction mixture, and the ethereal solution was washed first with dilute sodium hydroxide and then with water, dried over calcium chloride and the pasty mass obtained after removing ether was used for further reaction.

Rearrangement of o-Aroyloxyacetoarones into o-Hydroxydiaroylmethanes and cyclisation to Chromones.

2-(1'-Naphthyl) chromone :—

A mixture of o-(α-Naphthoyloxy) acetophenone (6 g.), pulverised sodium (1.5 g.) and dry toluene (30 cc.) was heated at 130°*C* for three hours and the separated yellow sodium salt was collected and first treated with alcohol to dissolve any excess of sodium and then acidified with dilute hydrochloric acid. *o*-Hydroxy-1'-naphthoylbenzoylmethane (4 g.) which separated was crystallised from glacial acetic acid in yellow crystals with m.p. 124°*C*. (Found : C, 78.7 per cent ; H, 5.1 per cent ; $C_{19}H_{14}O_3$ requires C, 78.6 per cent ; and H, 4.8 per cent). The solution of this substance (0.5 g.) in acetic anhydride (5 cc.) was treated with hydriodic acid (5 cc. ; d, 1.7) and kept overnight at room temperature. It was then poured into a cold saturated solution of sodium hydrogen sulphite and 2-(1'-naphthyl) chromone which separated was crystallised from alcohol in white crystals with m.p. 138-139°*C*. (Found: C, 84.1 per cent ; H, 4.7 per cent ; $C_{19}H_{12}O_2$ requires C, 83.8 per cent and H, 4.4 per cent).

2-(2'-Naphthyl) chromone:—

o-(β-Naphthoyloxy) acetophenone (6 g.) on treatment with pulverised sodium in dry toluene as described above gave o-hydroxy-2'-naphthoylbenzoylmethane (3.2 g.) crystallised from glacial acetic acid in yellow crystals with m.p. 141°*C*. (Found : C, 78.7 per cent ; H, 5.1 per cent ; $C_{19}H_{14}O_3$ requires C, 78.6 per cent and H, 4.8 per cent) ; which with hydriodic acid formed 2-(2'-naphthyl) chromone. It crystallised from alcohol with m.p. 134°*C*. (Found : C, 84.0 per cent ; H, 4.7 per cent ; $C_{19}H_{12}O_2$ requires C, 83.8 per cent and H, 4.4 per cent).

7-Hydroxy-2-(1'-naphthvl) chromone:—

A mixture of 4-benzoyloxy-2-(1'-naphthoyloxy) acetophenone (15 g.), pulverised sodium (0.8 g.) and dry benzene (40 cc.) was heated under reflux for four hours. In this reaction no solid sodium compound was separated but the whole reaction mixture formed a dark red solution. Benzene was removed from the reaction mixture by distillation and the yellowish red solid obtained was first treated with alcohol to dissolve any residual excess of sodium and then acidified with dilute hydrochloric acid. The separated 7-hydroxy-2-(1'-naphthyl) chromone (8.5 g.) crystallised from nitrobenzene with m.p. 291°*C* after sintering at 188°*C*. It is interesting to note that it exhibited intense red fluorescence with concentrated sulphuric acid unlike other chromones, and no fluorescence in alkali solution. It is insoluble in ether, cold or hot glacial acetic acid and in most of the common organic solvents. It gives no colouration with alcoholic ferric chloride. (Found : C, 79.2 per cent ; H, 4.2 per cent ; $C_{19}H_{12}O_3$ requires C, 79.2 per cent and H, 4.2 per cent).

7-Acetoxy-2-(1'-naphthyl) chromone prepared by the acetic anhydride-pyridine method, was crystallised from a mixture of absolute alcohol and benzene in white fine needles with m.p. 173°*C*. (Found : C, 76.4 per cent ; H, 4.2 per cent ; $C_{21}H_{14}O_4$ requires C, 76.4 per cent and H, 4.1 per cent). 7-Benzoyloxy-2-(1'-naphthyl) chromone prepared by the benzoylchloride-pyridine method, was crystallised from absolute alcohol with little benzene in white crystals with m.p. 159°*C*. (Found : C, 79.5 per cent ; H, 4.3 per cent ; $C_{26}H_{16}O_4$ requires C, 79.6 per cent and H, 4.1 per cent). Both the derivatives give intence red fluorescence with concentrated sulphuric acid as the original compound.

7-Hydroxy-2-(2'-naphthyl) chromone :—

4-Benzoyloxy-2-(2'-naphthoyloxy) acetophenone (12.5 g.) on treatment with pulverised sodium in dry benzene as described above gave benzoyl-4-benzoyloxy-2-hydroxy (2'-naphthoyl) methane (7.5 g.), crystallised from acetone in yellow crystals with m.p. 167-168°*C*. (Found : C, 76.1 per cent ; H, 4.2 per cent ; $C_{26}H_{18}O_5$ requires C, 76.1 per cent and H, 4.4 per cent). It gave a dark red colouration with alcoholic ferric chloride. This compound on refluxing with acetic anhydride and hydriodic acid formed 7-hydroxy-2-(2'-naphthyl) chromone. It crystallised from nitrobenzene with m.p. 288°*C*. (Found : C, 79.3 per cent; H, 4.2 per cent ; $C_{19}H_{12}O_3$ requires C, 79.2 per cent and H, 4.2 per cent). Benzoyl -4-benzoyloxy-2-hydroxy (2'-naphthoyl) methane (0.7 g.) on treatment with hydrogen bromide in acetic acid in the cold gave 7-benzoyloxy-2-(2'-naphthyl) chromone. It crystallised from a mixture of absolute alcohol and benzene in slightly cream coloured needles with m.p. 198°*C*. It exhibited blue fluorescence with concentrated sulphuric acid. (Found : C, 79.4 per cent ; H, 4.4 per cent ; $C_{26}H_{16}O_4$ requires C, 79.6 per cent and H, 4.1 per cent). 7-Acetoxy-2-(2'-naphthyl) chromone was prepared by the acetic anhydride-pyridine method. It crystallised from alcohol in white crystals with m.p. 190°*C*. (Found : C, 76.1 per cent ; H, 4.4 per cent ; $C_{21}H_{14}O_4$ requires C, 76.4 per cent and H, 4.1 per cent). It was insoluble in dilute sodium hydroxide but was soluble in concentrated nitric acid, giving yellow solution. It gave blue fluorescence with concentrated sulphuric acid.

7-Methoxyflavone :—

4-Methoxy-2-benzoyloxyacetophenone (0.8 g.) on treatment with pulverised sodium in dry benzene as described above gave a reddish oily product, which was extracted with ether and was converted to copper salt by shaking the ethereal extract with aqueous copper acetate solution. Greenish copper salt separated was washed first with ether and then with water. 2-Hydroxy-4-methoxydibenzoylmethane (4.2 g.) was separated by decomposing the copper salt with dilute hydrochloric acid. It crystallised from alcohol into fine shining yellow plates with m.p. 105°*C*. (Found : C, 70.9 per cent ; H, 5.2 per cent ; $C_{16}H_{14}O_4$ requires C, 71.1 per cent and H, 5.2 per cent). This on treatment with hydrogen bromide in acetic acid formed 7-methoxyflavone ; crystallised from alcohol into white needles with m.p. 110°*C*. It gave blue fluorescence with concentrated sulphuric acid. The compound has been prepared by Emilewicz and v. Kostanecki (Ber., 1899, *32*, 312) by the action of alcoholic potassium hydroxide on 4-methoxy-2-acetoxy-benezalacetophenonedibromide (m.p. 110-111°*C*). Turner and Robinson (J.C.S., *113*, 1918, 876) prepared it by the action of hydriodic acid on 2 : 4-dimethoxydibenzoylmethane (m.p. 110°*C*).

7-Methoxyflavone on treating with hydriodic acid formed 7-hydroxy. flavone. It crystallised from alcohol with m.p. 240°*C*. (Lit. m.p- 240°*C*).

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KOSTANECKI-ROBINSON REACTION

Part IV—Acetylation, Propionylation and Butyrylation of Orcpropio-phenone

By

P. L. TRIVEDI, S. M. SETHNA AND R. C. SHAH

IN continuation of the previous work (Sethna and Shah, J.I.C.S., 1940, *17*, 239, 487, 601), the Kostanecki-Robinson reaction has now been extended to the acetylation, propionylation and butyrylation of orcpropiophenone. The hitherto unknown orcpropiophenone has been prepared by Hoesch's method (Ber., 1915, *48*, 1127) for the preparation of orcacetophenone.

Kostanecki-Robinson reaction which consists in treating o-hydroxy ketones with sodium salts of fatty acids and their anhydrides gives either coumarins or chromones or a mixture of both depending on the ketone, the anhydride and the salt used. Thus, for example, resacetophenone or its mono-methyl ether gives on acetylation only a chromone whereas on propionylation and butyrylation it gives a mixture of chromones and coumarins, the latter being obtained in greater yield (Kostanecki and Rozycki, Ber., 1901, *34*, 102; Heilbron, Hey and Lythgoe, J.C.S., 1934, 1581; 1936, 297). Respropiophenone on acetylation gives exclusively a chromone (Canter, Curd and Robertson, J.C.S., 1931, 1262), but on propionylation and butyrylation of respropiophenone monomethyl ether the products obtained are mainly chromones with traces of the corresponding courmarins (Heilbron, Hey and Lythgoe, *loc. cit.*).

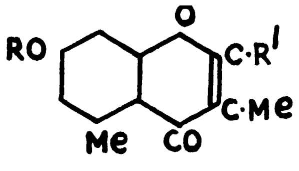
Orcacetophenone or its monomethyl ether however gave on acetylation, propionylation and butyrylation, 4-substituted c-acyl coumarins only (Sethna and Shah, *loc. cit.*). These compounds are of interest as their formation is noted for the first time. The 6-methyl group in orcacetophenone therefore seems to have a profound influence on the course of the Kostanecki-Robinson reaction. It was therefore thought of interest to study the acylation of orcpropiophenone.

Orcpropiophenone on acetylation and propionylation gave products to which structures of 7-acetoxy-2 : 3 : 5-trimethyl chromone (I, R= $COCH_3$ and R'=CH_3) and 7-propionoxy 2-ethyl-3 : 5-dimethyl chromone (I, R=COC_2H_5 and R'=C_2H_5) have beeen assigned. They gave no reaction with 2 : 4-dinitro phenyl hydrazene which indicated the absence of c-acyl group in 3-position. The above compounds on treatment with concentrated sulphuric acid gave products to which the structures of 7-hydroxy-2 : 3 : 5-trimethyl chromone (I, $R=H$, $R'=CH_3$) and 7-hydroxy-2-ethyl-3 : 5-dimethyl chromone (I, $R=H$, $R'=C_2H_5$) have been assigned as they were found to be identical on direct comparison with authentic specimens of these chromones prepared as described later.

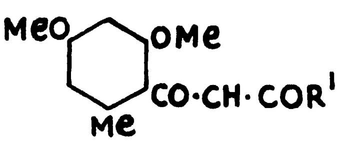
On butyrylation of orcpropiophenone, brown viscous mass was obtained which was directly treated with concentrated sulphuric acid when a product was obtained to which the structure of 7-hydroxy-2-propyl 3 : 5-dimethyl chromone (I, $R=H$, $R'=C_3H_7$) has been assigned as it was found to be identical on direct comparison with an authentic specimen of the same chromone. It did not react with 2 : 4-dinitro phenyl hydrazene thus indicating the absence of any c-acyl group in 3-position.

It has been thus found that the results are in general agreement with those of the previous workers who worked on other o-hydroxy propiophenones, *viz.*, that in acylation of o-hydroxy propiophenones, chromones are mainly or exclusively obtained (Canter, Curd and Robertson, *loc. cit.*; Heilbron, Hey and Lythgoe, *loc. cit.*). The results are however different from those obtained on similar acylation of orcacetophenone (Sethna and Shah, *loc. cit.*), when 4-substituted c-acyl coumarins were exclusively obtained. Thus the 6-methyl group in orcpropiophenone does not seem to have any marked influence on the course of the Kostanecki-Robinson reaction.

The chromones required in this work for comparison were prepared by the condensation of orcacetophenone dimethyl ether with ethyl acetate, ethyl propionate and ethyl butyrate respectively. The sodium salts of the B-diketones (II, $R=Na$, $R'=CH_3$, C_2H_5 and C_3H_7 respectively) so obtained were methylated with methyl iodide and the methylated B-diketones (II, $R=CH_3$; $R'=CH_3$, C_2H_5, C_3H_7 respectively) were treated with cold hydrobromic acid when methoxy chromones were obtained. These on heating with hydroiodic acid gave 7-hydroxy-2 : 3 : 5-trimethyl chromone, 7-hydroxy-2-ethyl 3 : 5-dimethyl chromone and 7-hydroxy-2-propyl-3 : 5-dimethyl chromone (I, $R=H$, $R'=CH_3$, C_2H_5 and C_3H_7 respectively).



(I)



(II)

EXPERIMENTAL

Preparation of orcpropiophenone (2 : 4-dihydroxy-6-methyl propiophenone).

It was prepared by Hoesch's method (Ber., 1915, *48*, 1127) for the preparation of orcacetophenone as follows :—

Anhydrous orcinol (60 g.) was dissolved in dry ether (150 cc.) and propionitrile (40 g.) and powdered $ZnCl_2$ (20 g.) added. Dry hydrogen chloride was passed through this for three hours and the reaction mixture kept overnight in frigidaire. A yellowish white mass separated the next day. After removal of ether the reaction mixture was treated with water and heated for 15 minutes. It was then cooled and treated with liquor ammonia till most of the hydrochloric acid was neutralised. It was then further heated for about 20 minutes. On cooling, reddish needles were obtained which were crystallised from hot water in long shining needles (20 g.) m.p. 127-128°. It gave dark red colouration with alcoholic ferric chloride. (Found : C, 66.5 per cent ; H, 6.8 per cent ; $C_{10}H_{12}O_3$ requires C, 66.6 per cent ; H, 6.6 per cent).

Acetylation of orcpropiophenone : 7-acetoxy-2 : 3 : 5-trimethyl chromone (I, R= $COCH_3$, R'=CH_3) (A).

Orcpropiophenone (2 g.) sodium acetate (6 g.) and acetic anhydride (20 cc.) were refluxed in an oil bath at 180-190° for 8-9 hours. The excess of acetic anhydride was distilled over and the reaction mixture added to water. The solid which separated was crystallised from alcohol in long wooly needles (1.5 g.) m.p. 122-123°. It was insoluble in cold dilute alkali and gave no colouration with alcoholic ferric chloride. (Found : C, 68.4 per cent ; H, 5.8 per cent ; $C_{14}H_{14}O_4$ requires C, 68.3 per cent ; H, 5.7 per cent).

7-hydroxy-2 : 3 : 5-trimethyl chromone (I, R=H, R'=CH_3) (B).

The above product (A) (1 g.) was kept for four hours with concentrated sulphuric acid (10 cc.) and then added to cold water. The product which separated was crystallised from alcohol in tiny needles (0.6 g.) m.p. 269-273°. Mixed m.p. with an authentic specimen of 7-hydroxy 2 : 3 : 5-trimethyl chromone prepared as described later was not depressed. It readily dissolved in cold dilute alkali and gave greenish blue fluorescence with concentrated sulphuric acid. No colouration with alcoholic ferric chloride was observed. (Found : C, 70.6 per cent ; H, 5.9 per cent : $C_{12}H_{12}O_3$ requires C, 70.6 per cent ; H, 5.9 per cent).

On treating the above products (A) and (B) separately with alcoholic potash (10 per cent) the product (B) was obtained from (A) and (B) remained unchanged. Also neither (A) nor (B) gave any 2 : 4-dinitrophenyl hydrazones, thus indicating the absence of c-acyl group in 3-position.

7-Methoxy-2 : 3 : 5-trimethyl chromone (I, R and R'=CH_3).

It was prepared by refluxing the product (B) (1 g.) dissolved in acetone (50 cc.) with methyl iodide (5 g.) in presence of potassium carbonate (2 g.). The product obtained after removal of acetone was crystallised from alcohol in prismatic needles (0.7 g.) m.p. 159°. Mixed m.p. with an authentic specimen of 7-methoxy-2 : 3 : 5-trimethyl chromone was not depressed. (Found : C, 71.4 per cent ; H, 6.6 per cent ; $C_{13}H_{14}O_3$ requires C, 71.6 per cent ; H, 6.4 per cent).

Propionylation of orcpropiophenone : 7-propionoxy-2-ethyl-3 : 5 : dimethyl chromone (C) (I, $R=COC_2H_5$; $R'=C_2H_5$).

Orcpropiophenone (2 g.) was refluxed with sodium propionate (6 g.) and propionic anhydride (20 cc.) in an oil bath at 180-190° for 8 hours. The excess of propionic anhydride was distilled over and the reaction mixture, after cooling, added to water. At first reddish yellow oil separated which on keeping in a frigidaire overnight solidified to a reddish yellow mass which was crystallised from alcohol in prismatic needles (1.2 g.) m.p. 75°. It was insoluble in cold dilute alkali and gave no colouration with alcoholic ferric chloride. (Found : C, 69'9 per cent ; H, 7.0 per cent ; $C_{16}H_{18}O_4$ requires C, 70.0 per cent; H, 6.6 per cent).

7-Hydroxy-2-Ethyl-3 : 5-dimethyl chromone (D) (I, $R=H$, $R'=C_2H_5$).

The above product (1 g.) was treated with concentrated sulphuric acid (10 cc.), kept for six hours and then poured in cold water. The product which separated was crystallised from alcohol in tiny needles (0.5 g.) m.p. 258-261°. Mixed m.p. with an authentic specimen of 7-hydroxy 2-ethyl 3 : 5-dimethyl chromone prepared as described later was not depressed. It was soluble in cold dilute alkali and gave greenish blue fluorescence with concentrated sulphuric acid. It did not give any colouration with alcoholic ferric chloride. (Found : C, 71.3 per cent ; H, 6.8 per cent ; $C_{13}H_{14}O_3$ requires C, 71.6 per cent ; H, 6.4 per cent).

On treating the above products (C) and (D) separately with alcoholic potash (10 per cent) the product (C) gave product (D) and the product (D) remained unchanged. Also none of the products gave 2 : 4-dinitrophenyl hydrazones. This indicated the absence of C-acyl group in 3-position.

The acetyl derivative, prepared as usual by heating with sodium acetate and acetic anhydride was crystallised from alcohol in tiny needles m.p. 107-108°. (Found : C, 68.8 per cent ; H. 6.6 per cent ; $C_{1}\,{}_{,}H_{16}O$ requires C, 69.2 per cent ; H, 6.1 per cent).

The methyl ether prepared as usual with methyl iodide and fused potassium carbonate was crystallised from alcohol in white tiny needles m.p. 130-131°. Mixed m.p. with an authentic specimen of 7-methoxy-2-ethyl-3 : 5-dimethyl chromone was not depressed. (Found : C, 72.2 per cent ; H, 7.2 per cent ; $C_{14}H_{16}O_3$ requires C, 72.4 per cent ; H, 6.9 per cent).

Butyrylation of orcpropiophenone : 7-hydroxy-2-propyl-3 : 5-dimethyl chromone (I, $R=H$; $R'=C_3H_7$).

Orcpropiophenone (2 g.), sodium butyrate (6 g.), and butyric anhydride (20 cc.) were refluxed in an oil bath at 180-190° for eight hours. On cooling, the reaction mixture was added to about a litre of cold water. Sodium bicarbonate solution was added slowly to neutralise butyric acid formed. Even on keeping in a frigidaire for four days the brown viscous oil obtained did not solidify, so it was taken up with ether. The ether extract was washed with sodium bicarbonate solution, dried and the ether evaporated. The brown oil thus obtained was directly treated with concentrated sulphuric acid (20 cc.) and kept for six hours. A yellow solid obtained on pouring the reaction mixture in cold water was crystallised from alcohol in shining needles (1 g.) m.p. 238-241°. Mixed m.p. with an authentic specimen of 7-hydroxy-2-propyl-3 : 5-dimethyl chromone prepared as described later was not depressed. It gave greenish blue fluorescence with concentrated sulphuric acid. It was soluble in cold dilute alkali and gave no colouration with alcoholic ferric chloride. (Found : C, 72.3 per cent ; H, 7.2 per cent ; $C_{14}H_{16}O_3$ requires C, 72.4 per cent ; H, 6.9 per cent).

It remained unchanged when treated with 10 per cent alcoholic potash. It also did not give a 2 : 4-dinitro phenyl hydrazone which indicated the absence of c-acyl group in 3-position.

The methyl ether prepared as usual with methyl iodide and fused potassium carbonate was crystallised from alcohol in small prisms m.p. 90°. Mixed m.p. with an authentic specimen of 7-methoxy-2-propyl-3 : 5-dimethyl chromone was not depressed. (Found : C, 73.0 per cent ; H, 7.7 per cent ; $C_{15}H_{18}O_3$ requires C, 73.2 per cent ; H, 7.3 per cent).

The acetyl derivative prepared as usual by refluxing the above hydroxy chromone with sodium acetate and acetic anhydride, was crystallised from alcohol in long needles, m.p. 95°. (Found : C, 69.6 per cent. ; H, 7.1 per cent ; $C_{16}H_{16}O_4$ requires C, 70.6 per cent ; H, 6.6 per cent).

(2' : 4' dimethoxy-6'methyl) benzoyl acetyl methyl methane (II, R=CH3 ; R' CH$_3$).

The sodium salt of (2': 4'-dimethoxy-6'-methyl) benzoyl acetyl methane (*cf.* Sethna and Shah, *loc. cit.*) was prepared by heating a mixture of orcacetophenone dimethyl ether (12 g.), ethyl acetate (22 g.) and pulverised sodium (3 g. approx. 2 mols) in an oil bath at 115-120° for an hour. Large excess of ether was added when the sodium salt got precipitated. This was filtered, washed free from tarry matter with ether, dried and then methylated by taking the sodium salt (10 g.) and heating it under reflux for five hours with methyl iodide (5.5 g.) in acetone (125 cc.). After removal of acetone, the residue was treated with water when a yellow oil separated, which did not solidify even on keeping it in frigidaire for 3 days. It was extracted with ether. The ether extract was dried and the ether evaporated when an oil was left behind. It gave violet colouration with alcoholic ferric chloride and was soluble in sodium hydroxide solution.

7-Methoxy-2 : 3 : 5-trimethyl chromone (I, R and R' =CH$_3$).

The above crude B-diketone (2 g.) was kept in contact with hydrobromic acid (d, 1.78 ; 7 cc.) for 24 hours and then poured in cold water. An orange coloured solid separated which was treated with sodium hydroxide (5 per cent ; 20 cc.) to remove demethylated chromone if any was formed. The alkaline solution on acidification however gave nothing. The insoluble portion in sodium hydroxide after thorough washing with water was crystallised from alcohol in long prismatic needles (0.8 g.) m.p. 159°.

7-Hydroxy-2 : 3 : 5-trimethyl chromone (I, R=H, R'=CH$_3$).

The above methyl ether (0.3 g.) was dissolved in acetic anhydride (3 cc.) and hydroiodic acid (d, 1.7 ; 5 cc.) added. The mixture was refluxed in an oil bath at 130-140° for two hours. The product obtained on adding the reaction mixture to sodium bisulphite solution was treated with sodium hydroxide (5 per cent ; 15 cc.). The insoluble portion was found to be the undemethylated methyl ether. The alkali soluble portion which came down on acidification with hydrochloric acid was crystallised from alcohol in woolly needles (0.13 g.) m.p. 269-273°.

(2'4'-dimethoxy-6'-methyl) benzoyl propionyl methyl methane (II, $R=CH_3$, $R'=C_2H_5$).

The sodium salt of the B-diketone-(2': 4' dimethoxy-6'methyl) benzoyl propionyl methane (*cf.* Sethna and Shah, *loc. cit.*) was prepared by heating a mixture of orcacetophenone dimethyl ether (10 g.), ethyl propionate (20 g.) and pulverised sodium (3 g.) in an oil bath at 115-120° for an hour. Large excess of ether was added when the sodium salt got precipitated. This was filtered, washed free from tarry matter by ether, dried and then methylated by taking the sodium salt (10 g.) and heating it under reflux for five hours with methyl iodide (5.5 g.) in acetone (125 cc.). After removal of acetone the residue was treated with water when a yellow oil separated which did not solidify even on keeping it in frigidaire for three days. It was extracted with ether. The ether extract was dried and the ether evaporated when an oil was left behind. It gave violet colouration with alcoholic ferric chloride and was soluble in sodium hydroxide solution.

7-Methoxy-2-ethyl 3 : 5-dimethyl chromone (I, $R=CH_3$; $R'=C_2H_5$).

The above crude B-diketone (2 g.) was kept in contact with HBr (d, 1.78 ; 7 cc.) for 24 hours and then poured in cold water. An orange coloured solid separated which was treated with sodium hydroxide (5 per cent ; 20 cc.) to remove demethylated chromone if any was formed. The alkaline solution yielded nothing on acidification. The insoluble portion was crystallised from alcohol in long prismatic needles (0.8 g.) m.p. 128-129°.

7-hydroxy-2-ethyl 3 : 5-dimethyl chromone (II, $R=H$, $R'=C_2H_5$).

The above methyl ether (0.5 g.) was dissolved in acetic anhydride (5 cc.) and refluxed with hydroiodic acid (d, 1.7 ; 5 cc.) in an oil bath at 130-140° for three hours. The product obtained on adding the reaction mixture to sodium bisulphite solution was treated with sodium hydroxide (5 per cent ; 15 cc.). The alkaline solution on acidification with hydrochloric acid gave brownish yellow mass which was crystallised from alcohol in small needles (0.3 g.) m.p. 258-260°.

(2'-4'-dimethoxy-6'-methyl) benzoyl butyryl methyl methane (II, $R=CH_3$; $R'=C_3H_7$).

The sodium salt of (2' : 4'-dimethoxy-6'-methyl) benzoyl butyryl methane (*cf.* Sethna and Shah, *loc. cit.*) was prepared by heating a mixture of orcacetophenone dimethyl ether (10 g.), ethyl butyrate (20 g.) and pulverised sodium (3 g.) in an oil bath at 115-120° for two hours. Large excess of ether was added to precipitate the sodium salt which was filtered, washed free from tarry matter with ether and dried. This was methylated by taking the sodium salt (10 g.) and heating it under reflux for five hours with methyl iodide (5 g.) in acetone (125 cc.).

After removal of acetone the residue was treated with water when a yellow oil separated which did not solidify even on keeping in a frigidaire for three days. It was extracted with ether, the ether extract dried and the ether evaporated. It gave intense violet colouration with alcoholic ferric chloride and was soluble in dilute sodium hydroxide.

7-Methoxy-2-propyl-3 : 5-dimethyl chromone (I, $R=CH_3$; $R'=C_3H_7$).

The above crude B-diketone (1.5 g.) was kept for 24 hours with hydrobromic acid (d, 1.78 ; 7cc.) and then poured into water when pasty mass separated which solidified after keeping it in a frigidaire overnight. It was treated with sodium hydroxide (5 per cent ; 10 cc.). The sodium hydroxide solution however did not yield anything on acidification. The insoluble portion after thorough washing with water was crystallised from alcohol in small prisms (0.6 g.) m.p. 91-92°.

7-hydroxy-2-propyl-3 : 5-dimethyl chromone (I, $R=H$; $R'=C_3H_7$).

The above methyl ether (0 5 g.) was dissolved in acetic anhydride (3 cc.) and refluxed with hydroiodic acid (d, 1.7 ; 3 cc.) for an hour in an oil bath at 130-140°. The product obtained on pouring the reaction mixture in sodium bisulphite solution was treated with sodium hydroxide (5 per cent ; 10 cc.). The product obtained on acidification of the alkaline solution with hydrochloric acid was crystallised from alcohol in tiny needles (0.15 g.) m.p. 238-241°.

One of us (S.M.S.) thanks the University of Bombay for the award of a research grant.

ROYAL INSTITUTE OF SCIENCE, BOMBAY;
AND
ELPHINSTONE COLLEGE, BOMBAY

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COMPARATIVE HYDROLYSIS OF PROTEINS FROM FOOD-GRAINS

By

N. V. BHIDE AND D. L. SAHASRABUDHE

IN all the civilized countries where scientific work is carried out there are laboratories which are specially devoted to the study of digestibilities of important food stuffs. In India a large amount of work on nutrition is being carried out at Coonoor, Bangalore, Madras, Calcutta, etc. The nutritive value of the food stuffs depends upon two factors, firstly the quantity of the essential constituents such as carbohydrates, proteins, fats, etc., which the food stuffs contain and secondly, how much of each becomes available to the body. The important constituents of a food stuff are carbohydrate, proteins, and fats. The study of the hydrolysis of the carbohydrates from various grains has been done by many workers, such as W. E. Stone (U.S.A. Dept. Agric. Bulletin, 1896, No. 34), C. F. Langsworthy (J. Biol. Chem., 1920, L. II), etc. Similarly the study of the proteins from the various grains has been carried out by using enzymes in-vitro or in-vivo by feeding the animals with the food stuffs. In India such studies have been made by Bhagwat and Shrinivasaya, (J. Ind. Inst. Sce., 1936, *19*A/10), Niogi, Narayana and Desai (Ind. Jour. Med. Res., 1931, *18*, 1217 ; *ibid*, *19*, 475 ; *ibid*, 1932, *19*, 859), Damodaran and Krishnaswami (Bio Chem. J. and Ind. Acad. Sc., 1942, XV, No. 6, 285-297), while among the workers in the foreign countries the names of Cohn and White (J. Bio. Chem. 1935, *109*, 169), Watermann and Johns (J. Bio. Chem. 1921, *47*, 285 ; 1923, *56*, 501) may be mentioned.

In order to get a general idea as regards the comparative digestibility of the food grains, it is necessary to study the rate of their hydrolysis by various hydrolysing agents. The authors have carried out experiments on the digestibility of various constituents of the important grains, but in this paper it is proposed to discuss the results of hydrolysis only of the proteins of the following grains :—

I *Cereals* :—(*a*) Bajri (Pennisetum typhoideum) ;
(*b*) Vari (Panicum milaceum).

II *Pulses* :— (*a*) Gram (Cicer arietinum) ;
(*b*) Black gram (Phaseolus radiatus).

HYDROLYSIS OF THE FLOURS WITH PEPSIN ONLY

Experimental :—Two grams of each of the flours were suspended in 25cc. of 0.1N. HCl and 25 cc. of 0.2% pepsin prepared in 0.1 N HCl were added to the suspension, it was then incubated at 37°C. for the required period, *i.e.*, one hour, two hours, and three hours. After the incubation for the fixed period five cc. of the 1 N NaOH were added to completely neutralise the acid ; and 5 cc. of the collodial iron were added to coagulate the proteins. 1 cc. of Magnesium Sulphate solution (50%) was added when complete coagulation took place and the solution became quite clear. The volume was made to 100 cc. and filtered. 5 cc. of the filtrate were used for the amino-nitrogen estimation by Van Slyke's Method (J. Biol. Chem., 1912, *12*, 399). The Hydrolysis was expressed in miligrams of nitrogen per 100 grams of the flour. A blank experiment was run side by side for every period and for every strength of the pepsin used and the result of the blank experiments together with the error of the apparatus were subtracted from the values obtained.

Of all the four flours Black-gram flour is the most attacked while the Vari flour is the least attacked. Between Bajri and Vari, Bajri flour is more easily attacked than the Vari flour.

The proportion of the proteins in pulses is as expected much more than in cereals. The striking difference between cereals and pulses is that, in cereals it takes a little time to start the hydrolysis and therefore the maximum nitrogen is liberated in the second period ; while in the pulses the proteins are all attacked from the very beginning.

The sudden drop in the rates of hydrolysis observed in the case of the cereals as well as pulses may be due to the fact that hydrolysis of the albumins and globulins takes place in two stages, during the first of which there is a rapid hydrolysis of the proteins to proteoses and peptones, while during the second stage the primary degradation products undergo a slow hydrolysis to similar products. An observation of this type has been made by McFartere (J. Gen. Physiol., 1927, *10*, 437). Miller and Calvery (J. Biol. Chem, 1936, *116*, 393) have found that the hydrolysis of lactalbumin by pepsin proceeds rapidly for the first few hours, 10.4% of the total nitrogen being liberated as amino nitrogen in four hours after which the rate decreases as the hydrolysis proceeds slowly for 66 days. The end products of the pepsin digestion of the proteins are mainly peptides of varying degrees of complexity, (Calvery and Schock, 1936, J. Biol. Chem., *113*, 15), although free amino acids may be liberated. So the complete digestion of the proteins does not take place in one stage. The end products of the pepsin digestion are further digested into simpler units by the enzymes of the alimentary cannal, which are secreted by pancreas.

TABLE NO. I

Hydrolysis of the Flours with 0.2%, 0.4% and 1% Pepsin expressed as Mg. of Nitrogen per 100 grams of the Flour

Name of the Flour	<—— 0 2% Pepsin		——>	<—— 0 4% Pepsin		——>	<—— 1% Pepsin		——>	Total Proteins %
	1 hour	2 hours	3 hours	1 hour	2 hours	3 hours	1 hour	2 hours	3 hours	
Bajri flour	72.46	217.4	338 1	217.4	279 6	360.8	212.4	280.1	380.5	9.6
Vari flour	51.77	165.7	176.0	113 9	209 0	248.5	123.5	218.7	273.09	7.53
Gram flour	383.1	424 5	486 6	372 8	476 2	517.7	517.5	600.5	673.0	20.03
Black-gram flour .. .	468.6	548 6	600 5	383.1	527 9	704.1	683.3	680.1	795.6	23.11

The digestion was therefore carried out by superimposed trypsin.

HYDROLYSIS OF FLOURS BY ENZYMES IN THEIR NATURAL SEQUENCE, *i.e.*, PEPSIN FOLLOWED BY TRYPSIN

Pancreas secrete three proteinases, Trypsin, Hytrotrypsin and Chymotrypsin : Several of the proteinases appear in the pancreatin juice in inactive form and require activation before they show their hydrolytic effect. The active enzyme is referred to as pancreatin proteinase or trypsin, trypsinkinse or trypsin. It is able to effect hydrolysis of high molecular weight proteins and protamimes. Calvery (1933, J. Biol. Chem., *102*, 73) has found that the enzyme is unable to bring about hydrolysis of albumin solutions in which pepsin digestion has previously been allowed to proceed to its maximum. Millar and Calvery (1936, J. Biol. Chem., *16*, 393) have found that trypsin is able to effect a slight further hydrolysis although the final degree of hydrolysis was approximately the same as when pepsin was allowed to proceed to its limit. So the pure pancreatin proteinase brings about the same amount of hydrolysis as pepsin.

In the light of these observations by the various workers on the proteins of the animal origin it was thought of interest to study the hydrolysis of the flours, subjected to successive action of pepsin and trypsin. This would provide the information as regards the behaviour of the proteins from vegetable origin.

Experimental :—The hydrolysis of the flours with the pepsin was carried out exactly as before. 50 cc. of 0.1 N HCl in the Pepsin digest were neutralised with 5 cc. of 1N. NaOH, and 5 cc. of 6% solution of trypsin in 0.1 N. NaOH were added, the resulting 60 cc. contained 0.5% trypsin and the hydroxyl ion concentration was 1/120. The activity of the enzyme was destroyed by heating the mixture at 80°C for 5 minutes. 5 cc. of colloidal Ferric Hydroxide and 1 cc. of 50% magnesium sulphate were added to clarify the mixture. The volume was made to 100 cc. and filtered, 5 cc. of the filtrate were used for the estimation of the amino nitrogen by Van Slyke's method.

The results are expressed as miligrams of nitrogen per 100 grams of the flour used. Digestion with 0.5% pepsin was allowed to proceed for 1 hour and then the same was used for the trypsin hydrolysis as described above.

TABLE No. 2

Milligrams of Nitrogen per 100 grams of the Flour for Superimposed Trypsin for 1 hour

Name of the Flour	mg. of N. for Pepsin	mg. of N. for Trypsin	Total. N. per cent
Bajri flour	217.4	288.8	9.6
Vari flour	113.9	155.3	7.53
Gram flour	372.8	538.3	20.03
Black-gram flour	508.1	512.9	23.29

The Gram flour is the most attacked by the superimposed trypsin while the Black-gram flour is the least attacked. In the case of the Gram flour the difference in amino nitrogen with the pepsin and the superimposed trypsin is 165.5 mg. of nitrogen while that for Black-gram flour the difference is only of 4.8 mg., *i.e.*, practically negligible. From this observation it seems that there is some fundamental difference in the nature of the proteins of the two pulses. Since the hydrolysis of the Black-gram flour with trypsin is slight it appears that the pepsin digestion has gone to such a stage that there is no further scope for the trypsin digestion. This is in the agreement with the observation made by Millar and Calvery (*loc. cit.*). So it may be concluded in the case of Black gram flour that the major amount of hydrolysis is due to pepsin only. While with Gram flour the tryptic hydrolysis is considerable.

In the cereals there is a considerable difference in the degree of hydrolysis by pepsin and trypsin digestion. The difference in the case of Bajri being more than that for Vari. Between Bajri and Vari, Bajri is more digestible under the influence of the proteolytic enzymes than the Vari flour, and between Gram and Black-gram, Black-gram is more digestible than the Gram flour.

SUMMARY

For the proteolytic disintegration two classes of grains were studied. The cereals contain comparatively a small percentage of proteins while pulse grains contain a high percentage protein.

(1) In the pulse flours pepsin brings about a large amount of hydrolysis of proteins and comparatively a small portion is left for being attacked by trypsin ; but in the case of cereal flours there is distinct difference between the degree of hydrolysis by that by pepsin and pepsin superimposed by trypsin.

(2) In the case of cereals it takes a little time to start the hydrolysis and therefore the maximum nitrogen is liberated in the second period, while in the pulse flours the proteins are attacked from the very beginning.

(3) The disintegration by pepsin superimposed by trypsin is maximum in the case of Gram flour while it is minimum in the case of Black-gram flour.

(4) The values of disintegration for Bajri flour obtained with pepsin and pepsin superimposed by trypsin are higher than those of Vari flour. Similarly the values of disintegration for the Gram flour are higher than those for the Black-gram flour.

(5) Between Bajri flour and Vari flour, Bajri flour is more digestible than Vari flour and between Gram flour and Black-gram, flour Black-gram flour is more digestible.

DEPARTMENT OF BIOCHEMISTRY,
N. WADIA COLLEGE,
POONA

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A PRELIMINARY NOTE ON THE PRESERVATION OF MILK WITH IODINE

By

I. D. Shiva Rao and Miss K. K. Tarachand

VARIOUS chemical methods of preserving fresh milk have been studied and all have been rejected as contrary to the health laws of any country. Recent literature, (The Chemical Analysis of Foods and Food Products, by Jacobs Morris), mentions also the use of iodine compounds as a simple preservative for food stuffs. This idea coupled with the fact that the addition of iodine to milk might prove a good method of administering iodine to individuals in inland places induced us to carry on a few experiments to study the effect of iodine on the storage of fresh milk as a food stuff.

In the preliminary stage we used iodine solution in the concentration of one gram in 100 cc. of one per cent potassium iodide solution, and one cubic centimeter was used for 100 cc. of milk. It was noticed that 4 cc. of the preservative could keep the milk fresh for nearly 275 hours at 7°C.

Next the effect of the preservative on the ferments of the digestive tract was studied. The extent of the action of amylase on starch was measured by the reduction of the cupric salt to the cuprous state, owing to the hydrolysis. 3 grams of amylum was emulsified in 100 cc. of distilled water, and to this one tablet of amylase was added, and this served as the control sample. In the other cases the volume was made up to 100 cc. with the varying quantities of iodine solution and distilled water. The samples were kept at 50°C for one hour. After the reaction, the solution was concentrated to one third the volume and the sugar estimated by Fehling's method. The results are given in the accompanying table :

Expt.	Control	0.04 gm. of I_2	0.06 gm. of I_2	0.08 gm. of I_2	0.10 gm. of I_2
I	0.195	0.152	0.117	0.096	0.07
II	0.166	0.151	0.099	0.079	0.05
III	0.142	0.133	0.124	0.123	0.07

The simple iodine solution has a slow depressant action on starch hydrolysis.

Peptic and Tryptic Digestion :—In the first case 20 cc. of 4% coagulated white of an egg in water was brought up to pH2, with the addition of either HCl or NaOH in drops. The flask was then kept in a thermostat at 40°C. 0.04 gm. of pepsin, (D.A.B.S., Merck), was added and the mixture diluted with 25 cc. of distilled water and the required quantity of iodine solution maintained at 40°C. For the purpose of estimating the hydrolysis, 5 cc. of the reaction mixture was withdrawn and 50 cc. of 95% alcohol was added to stop the reaction, and was then titrated with N/25 alcoholic potash. The experiment was repeated also with casein instead of the white of an egg. In the second case, that of tryptic digestion, the pH was maintained at 8.5 and 2 cc. of a phosphate buffer solution was added. The results of these hydrolytic estimations are given below :

White of an Egg			Casein		
Vol. of 1% I_2 sol.	Part hydrolysed in cc. of N/25 alc. KOH		Vol of 1% I_2 sol.	Part hydrolysed in cc. of N/25 KOH	
	Peptic dig.	Tryptic dig.		Peptic dig.	Tryptic dig.
0.0 cc.	0.55 cc.	0.82 cc.	0.0 cc.	. . .	2.5 cc.
0.2 cc.	0.49 cc.	0.79 cc.	0.2 cc	0.825 cc.	1.483 cc.
0.4 cc.	0.48 cc.	0.775 cc.	0.4 cc.	0.744 cc.	1.456 cc.
0.6 cc.	0.46 cc.	0.75 cc	0.6 cc.	0.738 cc.	1.349 cc.
0.8 cc.	0.44 cc.	0.745 cc.	0.8 cc.	0.702 cc.	1.311 cc.
1.0 cc.	0.42 cc.	0.65 cc.	1.0 cc.	0.676 cc.	1.095 cc
1.2 cc.	0.40 cc	0.61 cc.	1.2 cc.	0.66 cc.	1.08 cc.

Effect on the Composition of Milk :—Various estimations of the composition of milk, before and after varying additions of the preservative, were done. The chief results are given in the table below :

	Control	With 2 cc. of 1% I_2 for 50 cc. of milk	With 10 cc. of 1% I_2 for 50 cc. of milk
Water	83.8%	83.9%	83.9%
Total Solids	16.2%	16.1%	16.1%
Fat	7.2%	7.1%	5.1%
Ash	0.7%	0.7%	0.7%
Protein	3.8%	4.4%	4.0%
Lactose	4.5%	3.9%	4.8%

It is evident that there is no substantial change in the composition of milk owing to the addition of the perservative, except that a decrease in the fat contents is noted with high concentrations of the iodine solution.

Effect on the Vitamin Contents :—Tauber's method of estimating vitamin B_1 was used (mikrochemie Acta, 3, 108-9, 1938). The standard sample was the chloride Betaxin (Beyer's), each tablet containing 0.001 gram of the said vitamin. One tablet was dissolved in 100 cc. of distilled water. 0.2 cc. of this was further diluted to 1 cc. and was then treated with 0.5 cc. of 1% potassium ferrocyanide and 1 cc. of a fresh solution containing 30 grams of NaOH and 0.3 gm. of KCN in 100 cc. After shaking vigourously for about a minute, 1.5 cc. of 20 wt. per cent H_2SO_4 was added and then 5 cc. of ferric gum-ghatti solution. This latter was prepared by extracting 20 grams of gum-ghatti with water, and adding 5 grams of ferric sulphate and 25 cc. of 8% phosphoric acid in 100 cc. of water. This was the control sample.

In the case of milk, the organic matter was eliminated by oxidation with $KMnO_4$, which was added dropwise in a one per cent solution until the milk acquired a slight pink colour. Then 1.5 cc. of 20 wt. per cent sulphruic acid was added and the curdling was brought about. The serum of the milk with the sulphuric acid was then treated as in the case of the control sample. The colour comparison was done in the Dubosque comparator. The results were as follows :

Control Sample		With 4 cc. per cent		With 10 cc. per cent	
Standard	Milk Sol.	Standard	Milk Sol.	Standard	Milk Sol.
8	11	10	15.8	8	11

In the case of 4 cc. of the preservative a slight reduction in the vitamin value is noted.

Thus, iodine might serve as a helpful preservative in the case of fresh milk. The concentration as suggested by us is a bit too high compared with the maximum requirement of 200 micrograms. But it may actually help as a good source of iodine administration in food stuffs, especially in inland places.

St. Xavier's College,
Bombay

[*Received : July 7, 1942*]

CORRECTIONS

Pechmann Condensation of Phenols with Ethyl γ-Phenyl Acetoacetate

By

N. G. KOTWANI, S. M. SETHNA AND G. D. ADVANI

With reference to the above paper published in this Journal, Vol. X, Part 5, March 1942, certain mistakes crept in, which is regretted. The following corrections may, therefore, kindly be noted.

Page 144, line 12 from the bottom : *for* '2:4-Dimethyl β-benzyl cinnamic acid,' *read* '2:4-Dimethoxy β-benzyl cinnamic acid.'

do. 145, do. 27 from the top : *for* 'The acetyl derivative,' *read* 'The diacetyl derivative.'

do. 145, do. 30 from the top : *for* 'The methyl ether,' *read* 'The dimethyl ether.'

do. 145, do. 40 from the top : *for* 'The acetyl derivative,' *read* 'The diacetyl derivative.'

do. 146, do. 1 from the top : *for* 'The methyl ether,' *read* 'The dimethyl ether.'

do. 146, do. 4 from the top : *for* '2:4:6-Trimethoxy γ-benzyl coumarin,' *read* '2.4:6-Trimethoxy β-benzyl cinnamic acid.'

do. 146, do. 8 from the top : *for* 'α-Naphtha-4-benzyl coumarin,' *read* 'α-Naphtha-4-benzyl-α-pyrone.'

A NOTE ON A CALCAREOUS CONGLOMERATE IN BELGAUM DISTRICT

By

K. V. KELKAR AND L. V. AGASHE

THIS paper contains an account of an interesting calcareous conglomerate found among the superficial deposits occurring in the neighbourhood of Murgod in Belgaum District. The geology of the tract around Murgod (situated roughly between Longs. 74° 50′ and 75° 4′ east, and Lats. 15° 49′ and 15° 58′ north) may be described briefly as follows :—

The oldest rocks in the area form a part of the northern extremity of the main Dharwar band, and comprise shales, argillites and chloritic phyllites. A few epidiorites and hæmatite-quartzites occur also. Rarely thin bands of marble or calc-chlorite schist are found. To the east of the Dharwar rocks lies a massive granite-gneiss—a medium grained, grey coloured rock composed chiefly of acid plagioclase, microcline, quartz, and some hornblende and biotite.

Both, the Dharwar rocks and the granite-gneiss, are traversed by several small sized intrusions of granitic composition, or of pegmatite or vein quartz.

A few dykes of "Newer Dolerite" intersect the rocks previously mentioned. They are composed principally of labradorite and monoclinic pyroxene and accessory iron ore and quartz. The pyroxene is as a rule slightly uralitised.

Rocks of the Lower Kaladgi age occur in the eastern and the north-eastern parts. They include mainly quartzites and a few conglomerates succeeded by shales and limestones. These form a part of the southern edge of the central portion of the main Kaladgi Basin.

Deccan trap is chronologically the next formation. The variety found in this tract is dark grey coloured and porphyritic containing rather big phenocrysts of glass clear labradorite and rarely a few of small sized pyroxene. The aphanitic groundmass contains labradorite laths, granular enstatite-augite, accessory iron ore, glass and granules of altered olivine. A few vapour cavities and amygdales composed of zeolites, quartz, calcite, palagonite, etc., are present.

Finally come the superficial deposits like the soils, and several others which though varied in character have only a limited distribution and thickness. The latter include the well known deposits like kankar, the ferruginous material on the surface of the Kaladgi quartzites, the residual siliceous fragments covering the limestones and also the peculiar variety (calcareous conglomerate) described in this article.

A calcareous conglomerate is found occurring in close association with the Deccan trap or the soil resulting from it : it can be observed at Inchal, Harugop, Chachadi, Tadaslur, Halki and Budikop, and in fact at almost all places where Deccan trap occurs. It does not form extensive, continuous sheets but occurs in the form of scattered patches and small sheets, with a thickness varying between 6 inches and 2 feet. It usually occurs a few inches beneath the soil and may also be seen at the surface where the soil has been removed by natural or artificial causes.

The rock consists of material varying in size from pebble to sand, set in a fine textured or compact calcareous matrix. The pebbles are rounded to subangular and spheroidal, ellipsoidal or irregular in shape, and may attain a size of 3.5 cm. long and 2 cm. across. The cemented fragments may be of fairly uniform sizes, or they may be a heterogeneous aggregate of material of all grades from pebbles to coarse sand. Varieties with clastic grains of smaller size also occur and they resemble oolites and pisolites in appearance.

The pebbles and other clastic grains are generally calcareous and consist of micro-or crypto-crystalline aggregates of calcite ; there is usually no nucleus, and neither a concentric nor a radial arrangement is present. They occasionally show a rude concentric structure due to the presence of iron ore at the core or as a shell forming the marginal portion.

Some of the cemented fragments are non-calcareous and consist of gravel and sand from the adjacent soil ; they are generally heavily stained with ferruginous matter and look like red or brown jasper.

In thin sections the pebbles are translucent and red or yellow by transmitted light, or opaque and black or red by reflected light. Calcite occupies cracks and crevices in the pebbles, and in places it appears to have partially replaced the original material. Owing to the heavy ferruginous coating the source of the pebbles remains uncertain, but many can be recognised as fragments of Deccan trap and a few of the phyllitic and schistose rocks, etc., in the neighbourhood.

A small amount of quartz occurs in all rocks. It forms grains of small size only, much smaller than the calcareous fragments, and occurs either as inclusions in the calcareous grains or independently.

A few sand particles composed of hæmatite, limonite and ilmenite occur in all rocks, either as inclusions in the larger grains or in the material composing the matrix. The ores contain traces of manganese. Magnetite does not occur.

The matrix makes up nearly half of the rock and is composed almost entirely of calcareous matter, and all gradations between a matrix composed of turbid dust like calcite and a thoroughly crystalline fine grained matrix composed of close fitting, anhedral grains of calcite, are met with. In some rocks the matrix is thoroughly crystalline and the material composing the embedded pebbles is cryptocrystalline ; in others the revese is true.

By recrystallisation the fine calcareous dust has changed to granular calcite, and patches of recrystallised calcite may be seen in the cement as well as in the embedded fragments.

Chemical and microchemical tests show that the calcareous material is calcite, and that neither aragonite nor dolomite is present. None of the specimens answered the Heeger's test showing that they are altogether free from siderite.

The three specimens described below fairly represent the varieties found in this area.

No. 1. Locality—0/6 Mile ; Halki-Murgod Road

Reddish brown to dark pebbles, gravels, and sand ; individual grain 0.2 to 1.4 cm. in diameter ; set in grey or brownish grey calcareous matrix.

Microscopic

The clastic fragments consist of rock debris stained deeply by ferruginous matter, chiefly limonite and a little hæmatite. They are translucent to opaque, and yellow to red or deep reddish brown by reflected light. The translucent grains are red or brown by transmitted light. Cracks and cavities in grains have been filled up by calcite.

Some of the clastic grains have evidently been derived from Deccan trap : they are composed of much altered felspar, limonite and black opaque ore. The felspar has weathered beyond recognition and has been replaced in several places by calcite ; but its lath shaped form and the original structure of the basalt have remained in tact. The pyroxene has been replaced by hæmatite and limonite.

Majority of the grains are either heavily coated or replaced by ferruginous matter, and it is not possible to know their original character.

A few irregular grains of quartz are also present ; colourless and clear ; 0.25 to 0.5 mm. in diameter.

The matrix is composed of very finely divided calcite , it has a yellowish or browish tint due to ferruginous material. At places it has recrystallised yielding clear, transparent patches of granular calcite. The recrystallisation has taken place especially in portions close to the cemented grains.

No. 2. Locality—Budikop

A pale brown coloured rock ; gravels rounded or irregular ; varied sizes up to 1.6 cm. in diameter. The clastic material is usually grey, rarely brown or dark brown. The matrix is pale brown, and stands out prominently from the pale coloured clastic material.

Microscopic

Gravels composed generally of irregular aggregates of minute calcite granules. Rarely the individual granules have a diameter of 0.01 mm.; usually they are much finer. Quartz and iron ore occasionally occur as inclusions. There is no regularity in the arrangement of the component granules ; no nucleus, or radial or concentric arrangement is visible.

The rock contains a few fragments derived from some micaceous phyllite. They are usually stained by limonite ; but minute sericite wisps and quartz granules can be easily recognised. The structure of the original rock has been retained and the components show a distinct parallel grouping.

Several small sized, irregular or rounded grains of quartz and a few granules of iron ore occur.

The matrix is made up entirely of very finely divided calcite and is tinted yellowish brown. In places it has recrystallised yielding patches of coarse calcite granules. Some of the clastic grains and portions of the matrix have been stained yellow or reddish brown by limonite.

No. 3. Locality—Tadaslur

Rounded to subangular fragments of various sizes up to 1 cm. in diameter, embedded in a copious, fine textured, calcareous matrix. The cemented fragments are pink or pale to dark brown and their marginal portions have a deeper colour. The matrix is much paler than the embedded grains and yellowish grey.

Microscopic

The clastic grains have rounded or oval outlines. Many of them are composed chiefly of turbid calcareous dust and very fine calcite granules. In the majority of the fragments there is neither a nucleus nor a concentric or radial arrangement. A few have a nucleus or a large central patch of black iron ore. The ore also forms irregular patches within the spherical bodies. Dust like or granular ore is also enclosed by some grains and in places they form arborescent patterns. Minute quartz grains also occur as inclusions. The clastic grains are often tinted uniformly and in some cases the marginal portions have a deeper tint of yellow or brown limonite. The distribution of ferruginous matter gives a concentric structure to some of the pebbles.

The quartz grains are much smaller in size, up to 0.6 mm. across. They are clear and unstained. A few granules of opaque ore also occur as clastic grains ; some of them have changed into white leucoxene.

The matrix is much clearer, almost colourless, and composed of calcite which is much coarser than that of the clastic fragments and forms a mosaic of irregularly bounded close fitting grains.

Origin

The formation of the rock under consideration and of the other superficial deposits in this tract is determined or strongly influenced by the climate of the area. The climate may be summed up as a rainy season with a small amount of rainfall followed by a long dry season. Owing to the warmth or high temperature that prevails throughout the year, the water soaking into the rocks is fairly corrosive, and dissolves some components of the rocks through which it percolates. As the rainy season is followed by a long dry season, the ground water saturated with various salts is brought up to the surface by capillarity during the dessication period, and the material brought in solution is deposited at the surface or just beneath the soil as the water evaporates. The kankar in the trappean soil and the ferruginous material covering the Kaladgi quartzites have been formed in this manner. The materials brought to the surface may also cause metasomatic replacement of the superficial rocks ; as examples of such a process in this area may be cited the replacement of the sand-stone near Yerzarvi by hæmatite and the silicification of the shales near Budikop. The formation of the rock under consideration is due essentially to the same processes.

The rock apparently resembles oolites and pisolites which are formed by one of the following processes :—

1. By precipitation in shallow water when water saturated with calcium carbonate is in a state of gentle agitation.

2. In hot springs by deposition around grains which are buoyed up by the water.

3. Oolite-like rocks of mechanical origin : due to the accumulation of the pebbles of an older limestone. These are calcareous conglomerates and not true oolites or pisolites.

4. Oolitic structure also results when an emulsion crystallises, and some oolitic rocks may have originated in this way.

The mode of occurrence of the rock under consideration and the general geological history of the area rule out the possibility of the rock being either a lake or a spring deposit. The first three categories are thus eliminated.

The forms of the "pisolitic" grains and their internal structure show that the process summed up in the fourth category cannot account for the formation of this rock. The rounded bodies do not possess spherulitic structure of true oolites. They lack either a concentric or a radial structure, especially when they are made up of calcite alone. (Partial replacement of the marginal portion of a pebble by calcite or coloration of the marginal portion by limonite may produce an apparently concentric arrangement). Moreover the shape of the pebbles is not always spherical but many have the form of subangular pebbles of detrital origin.

The source of the calcium carbonate is obviously the lime-plagioclase from the Deccan basalt, which could supply abundant lime to the ground water ; and there is little doubt that the ascent of groundwater solutions to the surface by capillarity has been mainly responsible for accumulating the calcium carbonate near the surface. The formation of the rock is due to the action of calcium carbonate thus brought to the surface on a soil containing coarse sand and pebbles—at least a portion of the latter being detrital. The action of the carbonate has been two-fold : 1. Mere cementation, that is, deposition between the loose pebbles and formation

PLATE I

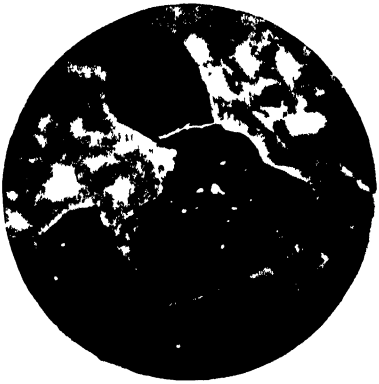

Fig. A

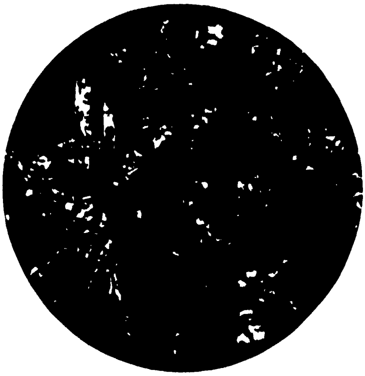

Fig. B

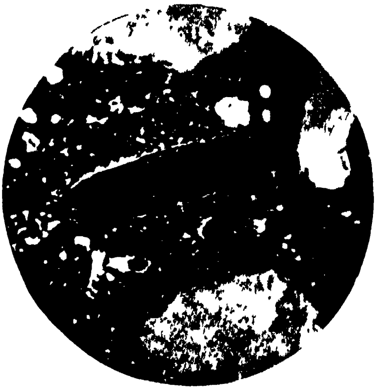

Fig. C

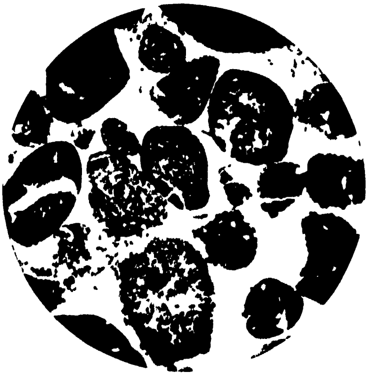

Fig. D

Fig E

of a conglomerate with a calcareous matrix ; and 2. Partial or complete replacement of the original pebbles in addition to the first process. Stated briefly, the rock has resulted by the cementation and metasomatic replacement of gravels in a trappean soil by calcareous solutions brought up to the surface by capillarity. The rock occurs mainly in the Deccan trap soil or close to it. Initially the soil contained pebbles and gravels derived mainly from the underlying Deccan trap and also a few washed from the adjacent Dharwarian phyllites and Kaladgi quartzites. Such fragments have subsequently been cemented and more or less replaced by calcite. Of the recognisable fragments the majority are derived from the Deccan basalt and a few from Dharwarian and Kaladgi rocks. Along with varieties that are almost entirely calcareous there also occur rocks containing a number of pebbles of non-calcareous material, such as fragments of basalt, phyllite etc. ; and all gradations between a conglomerate consisting of non-calcereous pebbles with calcareous cement and a calcareous conglomerate with calcareous pebbles and matrix are found.

EXPLANATION OF PLATE I

Photomicrographs

Fig. A. Specimen No. 1. Ordinary light, × 15.

The larger dark portions are the stained clastic grains ; the clear portions in them are cracks and cavities filled with calcite.

The rest of the portion is calcareous matrix ; the clear portions in it are patches of clear recrystallised calcite.

Fig. B. Specimen No. 1. Ordinary light, × 52.

A clastic grain derived from Deccan basalt showing weathered felspar laths, etc.

Fig. C. Specimen No. 2. Ordinary light, × 15.

Elongated grain at the centre derived from a phyllite. The larger grey patches are clastic grains replaced by calcite. The remaining material is calcareous matrix in which clear granules of quartz are seen.

Fig. D. A specimen from Halki. Ordinary light, × 15.

Iron coated clastic grains—black. Other clastic grains—dark or grey. Portions of clastic grains replaced by calcite—light. The clear matrix composed of calcite.

EXPLANATION OF PLATE II

Photograph

Fig. E. Natural size, showing some hand specimens.

FERGUSSON COLLEGE,
POONA

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TEMPERATURE DETERMINATIONS IN THEORY AND IN PRACTICE

By

N. R. TAWDE AND H. A. UNVALA,

Physics Laboratories, Royal Institute of Science, Bombay

OUR first conceptions of temperature are based on the physiological effect of heat. The sensations we feel when touching various objects give rise to such expressions as "hot," "lukewarm," "cold," etc. We also learn early that this peculiar property of a body is transmitted readily to other bodies in the vicinity and sometimes, even to those at a considerable distance. In a roundabout way, we realise that bodies placed together become equally hot or equally cold, which is the same thing as saying scientifically that they attain the same temperature. In fact, this is the basis of the various *Contact Methods* of measuring temperature.

However, our own sensations cannot be used to indicate or measure temperature to any great accuracy, as these are more or less qualitative, and depend upon previous experience. The well-known experiment of the three glasses of water, hot, cold and cool, has been so often cited in this connection that it need not be elaborated again here. In any case some objective means are necessary for the measurement of temperatures and the various methods that have been evolved to this end are briefly surveyed in this article.

The importance of accurate measurements of temperature cannot be stressed too much. In every branch of science and industry, nay even in every day life, temperature is of paramount importance for the simple reason that every process and reaction, physical, chemical or biological is affected by it to some extent or the other. This is most clearly evident in the mass production methods of modern industry in which rigid temperature control has to be maintained at every step of the manufacturing process to assure uniformity of the finished products. Actually some of the latest industries, such as those of plastics, were made possible only by the great improvements made in temperature measuring and controlling apparatus during comparatively recent times.

We are quite familiar with the reactions of our own body to changes in ambient temperature and find that in spite of its wonderful capacity for adjustment to large changes of such a nature, the body is able to work most efficiently only in a certain narrow range of temperatures. This has led to the development of air-conditioning, which depends for its efficient functioning on recently developed temperature controlling mechanisms.

Temperature control is equally important in the preparation of medicines and of various vaccines and serums, which cannot be produced to the required rigorous specifications without rigid control of temperature at every stage of the preparation.

To the physicist, chemist and technologist, the importance of accurate measurement and control of temperature is quite evident. To the astronomer and geologist, though control is impossible, measurement provides clues to various important problems such as the age of the stars and the earth.

In view of this great importance of temperature measurement, we give below in a classified form the various existing methods of measurement, our aim being to provide a comprehensive survey to those unfamiliar with the subject as a whole or as a part. Manifestly, it is impossible for a single person to be completely familiar with all the methods, and the most one can hope for is specialisation in a particular branch, but a general understanding of the whole subject is a preliminary requisite for a specialist and also helpful to others. Every attempt has been made to make the review as complete as possible, but in view of the enormous scope of the subject, it is likely that some methods might have escaped observation.

The various methods may be divided into two main classes, the *contact* and the *non-contact*, according as the testing body is, or is not placed in contact with the body under measurement.

1. *Contact Methods* :—In these the exchange of heat continues between the test body and the hot body, placed in contact with one another, till both attain the same temperature, which is indicated by one of its effects on the test body. These are as follows :

Class A. Thermal Expansion :—(i) of solids, (ii) of liquids, (iii) of gases.

In (i), we have the solid rod thermometers, metal coil thermometers and bimetallic strip, all expanding due to the heat on the familiar principle "heat expands and cold contracts," the expansion being measured by sensitive length-measuring methods or actuating an indicator over a graduated dial by suitable mechanical means. The familiar dial thermometers are of the latter type. This type is not susceptible to great accuracy.

(ii) As the expansion of liquids is not possible without some sort of containing vessel, this type divides into two sub-types, according as the liquid is in glass or in metal. The liquid-in-glass type is the one to which we are most familiar, the liquid being either mercury or coloured alcohol. Of this again there are different types such as the maximum and minimum thermometer, the clinical thermometer and Beckmann's thermometer. The last-mentioned is one of the most accurate measuring devices for small temperature variations.

(iii) Here the main sub-types are the constant pressure and constant volume gas thermometers. The closeness with which the so-called permanent gases obey the perfect gas law, makes this type particularly suitable for accurate measurements of temperature over a very wide range. The International Temperature Scale (I.T.S.) has been standardised by determining the location of a number of fixed points, such as the boiling points of oxygen and sulphur and the melting points of silver and gold under standard conditions on the Absolute Thermodynamic or Kelvin Scale, relative to the ice point, by means of gas thermometers. However, these are not very convenient in use and serve mainly as laboratory standards.

The expansion of a gas causes also a change in its density, which can be measured accurately by various methods, thus indirectly measuring the temperature. Change in density causes a change in refractive index which is measured by the displacement of the fringes in an interferometer pattern.[1] This method has been applied to the study of heat distribution in the neighbourhood of hot bodies, such as water-pipes and cylinders. The change in density has also been measured by X-Ray absorption,[2] alpha particle absorption[3] and electron absorption.[4] As the velocity of sound depends upon the gas density, the measurement of the velocity also provides a method of determining temperature.[5]

Class B. Thermo-electric Effect :—Methods utilising this effect are most widely used for determining high temperatures such as are encountered in industrial furnaces, and have been developed to a great degree of accuracy in this connection. These are subdivided into two classes, according as the metals used for the junctions are rare or base metals. Thermocouples of rare metals are not so readily affected by the outside conditions and serve as good standards. However, in the extreme furnace conditions, depreciation does occur and base metal couples are also used, due to the cheapness with which they can be replaced. The thermocouples can be made so small in size as to be suitable for measurements of surface temperatures, and have been thus used in measuring skin temperatures of various animals and of the human body by physicians.

Class C. Change in Electrical Resistance :—This property is made use of in the resistance thermometers in which the change of resistance is most generally measured by highly improved forms of the Wheatstone network. For platinum, the relation between the temperature and resistance is a very regular one, and so this is the material almost universally used in resistance thermometers, considerable accuracy being attainable. Another form of thermometer utilising this property is the electrolytic thermometer used in Radiosondes,[6] which are light instruments, sent aloft by a free balloon and transmitting radio signals which can be interpreted in terms of the pressure, temperature and humidity of the upper air. The thermometer consists of a fine capillary, containing the electrolyte, the resistance of which varies much with changes of temperature. This resistance controls the frequency of modulation of the special audio-oscillator and the signals of this frequency received at the ground can be converted to the appropriate temperature values.

Class D. Change in Magnetic Susceptibility :—This method[7] is used for the measurement of the extremely low temperatures (below 1°K) obtained by magnetic cooling methods. When paramagnetic salts, previously cooled, are subjected to intense magnetic fields, their temperature drops very much reaching within a fraction of a degree of the Absolute Zero (0° K or -273°C) of temperature. At the same time, the magnetic susceptibility changes rapidly, and, on being measured provides a method of measuring the temperature.

Class E. Change of State of Test Body :—Substances of fixed melting and boiling points provide us with a discontinuous but accurate scale of temperature. Thus, the International Temperature Scale, as mentioned earlier, is based on a certain number of such points. In measuring furnace temperature, rings of different metallic alloys with graded melting points are used. The pyrometric cones,[8] extensively used in the ceramic industry, are slender pyramids of a mixture of minerals similar to the composition of ceramic bodies and with graded melting points at approximately 20°C intervals. These are fired in furnaces along with the ceramic ware and their deformation is an indication of the ware having been fired sufficiently for maturity. The various strata of the earth's crust are also, to an extent, thermometers of this type as the phase changes of the minerals enable the geologist to determine the various temperatures undergone by the constituents.

Class F. Calorimeter Pyrometers :—In these the test body has a large heat capacity and the change in its heat content on immersion of the body under measurement, enables a calculation of its temperature to be made.

Class G. Special Methods Designed to Obtain Temperature Equilibrium Between Hot Body and Test Body :—These are mainly applied in gas temperature measurements because the test body receives heat not only by convection from the gas but also by radiation from the walls of the containing chamber. If these walls are at a temperature different from that of the gas, the true temperature will not be indicated. In the Suction Pyrometer of High Velocity Thermocouple[9] the hot gas is aspirated at high velocity past the thermocouple, thus establishing temperature equilibrium between it and the gas. In the Heated Plate method[10], a plate or wire of platinum in the gas is supplied extra heat electrically. If the platinum is colder than the gas flame, soot will form on it; if hotter, it will not. The temperature at which soot just forms gives the true gas temperature. This is essentially a laboratory method. The Heated Wire and Vacuum Calibration[11] methods make use of the fact that under steady conditions, a heated wire in a gas or in a vacuum loses or gains heat by radiation and by conduction to supports, and only when its temperature is different from that of the gas, also by convection to the gas. Thus for a wire in a gas at the same temperature, the heat loss or gain conditions are identical to those in vacuum, and so the point at which the current and the temperature are the same for both the wires is the true gas temperature.

2. *Non-Contact Methods* :—In these, the test body is placed at a distance from the body under measurement and consists of some form of radiometer. These are generally useful for determining surface temperature of liquids and solids and indirectly for the temperature of a gas by means of a body placed inside it, and are the only methods of temperature measurement useful to the astronomer.

Class A. Black Body Radiation Measurements :—Radiation from hollow bodies confirm to blackbody conditions or the existing surfaces inside furnaces, etc., can be taken as near approximations, in certain cases.

(i) *Total Intensity Radiometers*[12] :—These make use of the Stefan-Boltzmann law. The radiometer consists of a thermojunction, a bimetallic strip or a resistance thermometer, and measures the total energy in the spectrum emitted by the blackbody. A well-known type is the Féry radiation pyrometer.

(ii) *Optical Pyrometers*[12] :—In these, the energy emitted in a particular portion of the spectrum is measured by matching the brightness in that portion with the brightness of a filament in which the current is varied or of a field which is gradually dimmed by optical wedges or polarising nichols

(iii) *Photoelectric Pyrometers*[12] :—The incident energy is measured by photoelectric devices such as photoelectric tubes and rectifier-type cells. However, as these are selective in spectral response, they have to be calibrated first to determine the non-uniform way in which the response varies with the temperature.

Class B Grey Body Temperature Measurements —A grey body is one in which the spectral intensity distribution is relatively the same as that of a blackbody. In Colour Pyrometers, the intensities emitted at two different wavelengths are compared and the temperature obtained by solving the simultaneous Planck's or Wien's equations [13]

Class C Electronically Excited Radiation from Solids and Gases —As the intensities and intensity-distributions in spectra are dependent on the temperature of the emitters, the determinations of these give clues to the temperature In the Line Reversal method, the brightness of the line is measured by matching it with the known brightness at the same wavelength in a blackbody spectrum If the temperature of the blackbody is low the line appears brighter by comparison, if the temperature is higher the line appears dark, the temperature of the blackbody at which this reversal takes place and the line becomes invisible is called the reversal temperature, and if the line radiation is of a thermal character this is also the temperature of the line-emitting source [14]

The measurement of intensity-distribution in the rotational or vibrational levels of band spectra is also an important means of determining the temperature of sources emitting such radiation The relative intensities in the spectrum are dependent upon the temperature and this relation enables the temperatures of the sources to be determined[1] from relative intensity measurements

Probe Method —The very high electronic temperatures in the interior of gaseous discharge are estimated by the method of probe measurements The probe consists of a small electrode extending into the discharge and the temperature is calculated from the current-voltage relation of the probe.

It would be interesting to quote here the limits of temperature known to science The lowest temperature theoretically is the absolute zero of the Kelvin scale or approximately —273°C or O°K. By methods of magnetic cooling, 0·001°K has been reached in the laboratories of the University of Leyden, Holland. The highest temperature generally used for heating purposes in laboratories and industrial furnaces is somewhere above 3000°C. The highest temperature attained so far on the earth is about 10,000°C, the temperature inside a 10-ampere arc under a pressure of 1,000 atmospheres. Temperatures far above these are to be found in the starry heavens—the cosmic laboratory of the universe. The surface temperatures of the type 05 stars are as high as 80,000°C, whereas within their interiors the temperatures are still higher. It has been calculated that in the interior of a sub-dwarf star the temperature is above 50,000,000°C.

These are the principal methods adopted in determinations of temperature. Some of these can only remain in the laboratory stage, but most have been already developed for industrial use. With the progress of research, it is quite likely that new methods hitherto unknown may be found and adopted for practical purposes, for general or particular use.

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SCIENCE NOTES

On the Corrections of the Compound Pendulum

By

B. N. Biswas

Rajaram College, Kolhapur

THE relation between the modified time period of a compound pendulum and its amplitude which is supposed to be a small finite quantity has been deduced here by the method of successive approximation, and a formula has also been evolved connecting the computed time of the pendulum and all the four corrections.

Before solving the main problem directly it is advantageous to solve the differential equation,

$$\frac{d^2\theta}{dt^2}+n^2\theta = A\cos pt \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

representing the forced oscillation of a body.

The solution consists of two parts of which one is obtained by putting $\frac{d^2\theta}{dt^2} n^2\theta = 0$ and is known as the complementary function and the other known as the particular solution which satisfies (1) completely.

The most general solution of the equation

$$\frac{d^2\theta}{dt^2}+n^2\theta = 0 \text{ is } \theta = A.\cos nt + B.\sin nt \quad \ldots \quad . \quad \ldots \quad (2)$$

where A and B are two arbitrary constants which can be evaluated in terms of initial displacement and initial velocity.

If θ_0 and $\dot{\theta}_0$ denote the initial displacement and initial velocity respectively, equation (2) can be written in the following form :

$$\theta = \frac{\dot{\theta}_0}{n}\sin nt + \theta_0 \cos nt \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

Equation (3) may now be employed to obtain the solution of the complete equation (1).

From (3) it is clear that the effect at time t due to imparting a velocity $\delta\dot{\theta}$ at time t′ is,

$$\theta = \frac{\delta\dot{\theta}}{n} \sin n\,(t-t') \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

The effect of the term A. cos pt is to produce a velocity =A. cos pt'. dt′ at time t′, whose effect at time t will be,

$$\theta = \frac{A.\ \cos pt'\ dt'}{n}.\ \sin n\,(t-t')$$

If the term be operative for the whole of the time, from t′=o to t′=t, the value of θ at time t is given by,

$$\theta = \frac{A}{n}\int_{o}^{t} \sin n\,(t-t').\ \cos pt'.\ dt' \quad . \quad \ldots \quad \ldots \quad (5)$$

$$= \frac{A}{2n}\int_{o}^{t} [\sin \{t'\,(p\text{-}n)+nt\} + \sin \{t'\,(-p\text{-}n) + nt\}]dt'$$

$$= \frac{A}{2n}\left[-\frac{\cos \{t'\,(p\text{-}n)\ +nt\}}{p-n} + \frac{\cos \{t'\,(-p\text{-}n) + nt\}}{p+n}\right]_{o}^{t}$$

$$= -\frac{A}{p^2-n^2}\cos pt + \frac{A}{p^2-n^2}\cos nt \quad \ldots \quad \ldots \quad (6)$$

From (6) it is obvious that θ and $\dot{\theta}$ are each equal to zero at time t=o and the complete solution of equation (1) is,

$$\theta = \frac{\dot{\theta}_o}{n}.\ \sin nt + \left(\theta_o + \frac{A}{p^2-n^2}\right).\ \cos nt \cdot \frac{A}{n^2-p^2}\cos pt \quad \ldots \quad (7)$$

where $\dot{\theta}$ and θ denote the velocity and displacement at time t=o.

The solution of the equation of the type

$$\frac{d^2\,\theta}{dt^2} + n^2\theta = A_1 \cos p_1 t + A_2.\ \cos {}_2pt \quad . \quad \ldots \quad \ldots \quad (8)$$

can also be found by pursuing the method illustrated above in the manner suggested below.

The equation is broken into the following parts and the solution of each part is obtained separately. The complete solution is the sum of all these individual solutions.

Thus the solution of

i) $\dfrac{d^2\,\theta}{dt^2} + n^2\theta = A_1 \cos p_1 t$ is $\dfrac{A_1}{n^2\ p_1{}^2}\cos p_1 t - \dfrac{A_1}{n^2-p_1{}^2}\cos nt$

ii) $\dfrac{d^2\,\theta}{dt^2} + n^2\theta = A_2 \cos p_2 t$ is $\dfrac{A_2}{n^2-p_2{}^2}\cos p_2 t - \dfrac{A_2}{n^2-p^2{}_2}\cos nt$

Hence the complete solution of (8) is,

$$\theta = \frac{\dot{\theta}_o}{n} \sin nt + \left(\theta_o - \frac{A_1}{n^2-p_1{}^2} - \frac{A_2}{n^2-p_2{}^2}\right) \cos nt$$

$$+ \frac{A_1}{n^2-p_1{}^2} \cos p_1 t + \frac{A_2}{n^2-p_2{}^2} \cos p_2 t \quad \ldots\ldots\ldots \quad (9)$$

Amplitude correction.

Equation of motion of the pendulum is,

$$\text{I.} \quad \frac{d^2\theta}{dt^2} = - \text{mgl. } \sin \theta = -\text{mgl} \left(\theta - \frac{\theta^3}{6}\right) \ldots \text{ if } \theta \text{ be small.}$$

$$\text{or } \text{m}\left(\text{k}^2 + l^2\right) \frac{d^2\theta}{dt^2} = - \text{mgl.} \left(\theta - \frac{\theta^3}{6}\right)$$

$$\text{or } \frac{d^2\theta}{dt^2} + \frac{gl}{k^2+l^2}\theta = \frac{gl}{k^2+l^2} \frac{\theta^3}{6} \quad (10)$$

where m denotes the mass of the pendulum, k, the radius of gyration about a parallel axis through its centre of gravity, l, the distance of its centre of gravity from the point of suspension and *g*, the acceleration due to gravity.

Let us assume that an approximate solution is $\theta = A \cos mt$ (11) with a suitable value for *m* which is slightly different from $\sqrt{\frac{gl}{k^2+l^2}}$. For, it is evident beforehand that the period, corresponding to the equation $\frac{d^2\theta}{dt^2} + \frac{gl\theta}{k^2+l^2}$ 0. is slightly modified in view of the fact that the acceleration corresponding to θ is slightly different from $\frac{gl\theta}{k^2+l^2}$ and that it has got the same value at the same position on the other side of the equilibrium position.

On substituting the value of θ as given by (11) in the right side of (10) we get,

$$\frac{d^2\theta}{dt^2} + \frac{gl\theta}{k^2+l^2} = \frac{gl}{k^2+l^2} \frac{A^3 \cos^3 mt}{6} \quad \ldots\ldots \quad (12)$$

$$\cos^3 mt = \frac{\cos 3mt + 3.\cos mt}{4} \quad \ldots\ldots \quad (13)$$

From (12) and (13) we get,

$$\frac{d^2\theta}{dt^2} + \frac{gl\theta}{k^2+l^2} = \frac{gl\,A^3}{24\,(k^2+l^2)} [\cos 3\,mt + 3 \cos mt]$$

$$= \frac{3\,gl\,A^3 \cos mt}{24\,(k^2+l^2)} + \frac{gl\,A^3 \cos 3\,mt}{24\,(k^2+l^2)} \quad \ldots\ldots \quad (14)$$

On putting $n^2 = \frac{gl}{k^2+l^2}$ in (14), it becomes,

$$\frac{d^2\theta}{dt^2} + n^2\theta = \tfrac{1}{8}\, n^2 A^3 \cos mt + \frac{A^3 n^2}{24} \,.\, \cos 3\, mt \qquad \ldots \qquad \ldots \quad (15)$$

The solution of (15) in view of (9) is,

$$\theta = \tfrac{1}{8}\, n^2 \frac{A^3}{n^2-m^2} \cos mt + \frac{A^3 n^2}{24} \frac{\cos 3\, mt}{n^2-9\, m^2} \qquad \ldots\ldots \quad (16)$$

The solution consists of two terms, the first of which is equal to A. cos mt in view of (11) while the second is the correction term to be added to A cos mt to get a nearer solution.

$$\text{Hence } A = \tfrac{1}{8} \frac{n^2 A^3}{n^2-m^2}$$

$$\text{or } m^2 = n^2 - \tfrac{1}{8}\, n^2 A^2$$

$$\text{Modified period} = \frac{2\pi}{m} = \frac{2\pi}{n\left(1-\frac{A^2}{8}\right)^{\frac{1}{2}}}$$

$$= \frac{2\pi}{n}\left[1 - \tfrac{1}{8} A^2\right]^{-\frac{1}{2}}$$

$$= \frac{2\pi}{n}\left[1 + \frac{1}{16} A^2\right] \qquad \text{as A is small}$$

$$= 2\pi \sqrt{\frac{k^2+l^2}{l.g}} \left(1 + \frac{A^2}{16}\right) \qquad \ldots\ldots \quad (17)$$

on putting the value of n.

Relation between the computed time of the pendulum and all the four corrections taken together

T_1 = time period of the pendulum corresponding to infinitely small amplitude in the erect position.

T_2 = time period of the same in the inverted position.

l_1 = distance of the C G. of the pendulum from the knife-edge in the erect position.

l_2 = distance of the C.G. of the pendulum in the inverted position from the second knife-edge.

Let us put

$$T^2 = \frac{T_1^2 .\, l_1 - T_2^2 .\, l_2}{l_1 - l_2} \qquad \ldots\ldots \quad (18)$$

where T is defined to be the computed time of the pendulum.

BESSEL'S equation for determining "g".

$$\frac{g}{4\pi^2} T^2 = \frac{g}{4\pi^2} \left\{ \frac{T_1^2 .\, l - T_2^2 .\, l_2}{l_1 - l_2} \right\} = l_1 + l_2 \qquad \ldots\ldots \quad (19)$$

Equation (19) has been derived on the assumptions that amplitude of the pendulum is vanishingly small, that it oscillates in vacuum, that the knife-edges are perfectly sharp and that the point of support is absolutely at rest throughout the motion. As these assumptions are only approximately true, corrections are necessary. There are four corrections corresponding to four sources of error as given below :

1. *Amplitude correction.*

$$\frac{g}{4\pi^2}T^2=\frac{g}{4\pi^2}\left\{\frac{T_1^2\left(1-\frac{a_1^2}{16}\right)l_1-T_2^2\left(1-\frac{a_2^2}{16}\right)l_2}{l_1-l_2}\right\}$$

$$=l_1+l_2 \quad \cdot\cdot \quad \cdot\cdot \qquad (20), \text{ from } (17) \text{ and } (19)$$

where T_1 and T_2 denote the observed time periods and a_1 and a_2 the corresponding amplitudes in the erect and inverted position respectively, it being supposed that other three sources of error are absent here.

2. *Correction for buoyancy and inertia of air.*

Instead of oscillating in vacuum, if the pendulum vibrates in air Bessel's equation for g, after taking into account this source of error is written in the following form :

$$\frac{g}{4\pi^2}T^2=\frac{g}{4\pi^2}\left\{\frac{T_1^2.\,l_1-T_2^2.\,l_2}{l_1-l_2}\right\}$$

$$=l_1+l_2+\frac{m'}{m}\frac{L}{l_1-l_2}(s_1-s_2)+\frac{i_1-i_2}{m(l_1-l_2)} \quad \ldots \quad (21)$$

where m' mass of air displaced by the pendulum ;

m=mass of the pendulum ;

i_1 - increase in the moment of inertia of the pendulum in the erect position due to air carried along with it ;

i_2 — same in the inverted position ;

s_1 distance of the centre of figure from the point of suspension ;

s_2 = same from the centre of oscillation ;

$$L=\frac{k^2+l_1^2}{l_1}=\frac{k^2+l_2^2}{l_2}$$

—length of equivalent simple pendulum, other three sources being assumed to be absent.

3. *Knife-edge correction.*

$$\frac{g}{4\pi^2}T^2=\frac{g}{4\pi^2}\left\{\frac{T_1^2.\,l_1-T_2^2.\,l_2}{l_1-l_2}\right\}$$

$$=l_1+l_2+\frac{L}{l_1-l_2}(r_2-r_1) \quad \cdot\cdot \quad \cdot\cdot \qquad (22) \text{ (Bessels' formula).}$$

r_1 = radius of curvature of the cylindrical surface of the first knife-edge (erect position).

r_2 = same of the second knife-edge (inverted position).

4. *Correction due to the yielding of the point of support.*

$$\frac{g}{4\pi_2}T^2 = \frac{g}{4\pi^2}\left\{\frac{T_1^2 \,.\, l_1 - T_2^2 \,.\, l_2}{l_1 - l_2}\right\} = l_1 + l_2 + mg\,\alpha \ldots \quad (23)$$

where α = horizontal displacement of the point of support per unit force.

It will be shewn now that if all the sources of error are simultaneously present, the resultant correction is the sum of the individual corrections mentioned above.

Equation of motion of the pendulum, taking into consideration the finiteness of the amplitude, which is small, buoyancy and inertia of air and curvature of the knife-edge is,

$$(I+i)\frac{d^2\theta}{dt^2} = -\left\{mg\,(l+r) - m'g\,(s+r)\right\}\left(\theta - \frac{\theta^3}{6}\right) \ldots \quad (24)$$

where m, m', r and i have their usual meanings, m', r and i are supposed to be small,

$$I = m\,(k^2 + l^2) \quad \ldots\ldots \quad (25)$$

On putting $k = \frac{g}{(I+i)}\left\{m\,(l+r) - m'(s+r)\right\}$ …… (26)

in (24) we get,

$$\frac{d^2\theta}{dt^2} = -k\left(\theta - \frac{\theta^3}{6}\right) \quad \ldots\ldots \quad (27)$$

T = time period $= \frac{2\pi}{\sqrt{k}}\left(1 + \frac{a^2}{16}\right)$ …… (28)

where a is the amplitude in view of (17).

From (26) and (28) we get,

$$\frac{g}{4\pi^2}T^2\left(1 - \frac{a^2}{16}\right)^2 = \frac{m(k^2+l^2)+i}{m(l+r) - m'(s+r)} = \frac{k^2+l^2+\frac{i}{m}}{l+r-\frac{m'}{m}(s+r)}$$

$$= \frac{k^2+l^2+\frac{i}{m}}{l+r}\left(1 + \frac{m'}{m}\frac{(s+r)}{(l+r)}\right) \quad \text{approx.}$$

$$= \frac{k^2+l^2}{l+r} + \frac{k^2+l^2}{l+r} \cdot \frac{m'}{m}\frac{s+r}{l+r} + \frac{i}{m(l+r)} \quad \text{approx.}$$

$$=\frac{k^2+l^2}{l}\left(1-\frac{r}{l}\right)+\frac{k^2+l^2}{l}\frac{m'}{m}\frac{s}{l}\left(1+\frac{r}{s}\right)\left(1+\frac{r}{l}\right)^{-2}$$
$$+\frac{i}{ml}\left(1-\frac{r}{l}\right)$$

$$=\frac{k^2+l^2}{l}-\frac{k^2+l^2}{l}\cdot\frac{r}{l}+\frac{k^2+l^2}{l}\frac{m'}{m}\cdot\frac{s}{l}+\frac{i}{ml} \qquad \ldots\ldots \quad (29)$$

approximately, neglecting terms of the order $m'.\,r$.

The effect of the yielding of the point of support is equivalent to increasing the length by δ, where

$$\delta=\frac{\alpha.mgl^2}{k^2+l^2} \qquad \ldots\ldots \quad (30)$$

Its effect on S. upto a first approximation can be neglected.

From (29) we get,

$$\frac{g}{4\pi^2}\mathrm{T}^2\left(1-\frac{a^2}{16}\right)^2$$
$$=\frac{k^2+(l+\delta)^2}{l+\delta}-\frac{k^2+(l+\delta)^2}{(l+\delta)^2}r+\frac{k^2+(l+\delta)^2}{(l+\delta)^2}\frac{m'}{m}s+\frac{i}{m(l+\delta)}$$
$$=\frac{k^2+l^2+2l\delta}{l}\left(1-\frac{\delta}{l}\right)-\frac{k^2+l^2+2l\delta}{l^2}\left(1-\frac{2\delta}{l}\right)r$$
$$+\frac{k^2+l^2+2l\delta}{l^2}\left(1-\frac{2\delta}{l}\right)\times\frac{m'}{m}s+\frac{i}{ml}\left(1-\frac{\delta}{l}\right)$$
$$=\frac{k^2+l^2}{l}-\frac{k^2+l^2}{l}\cdot\frac{\delta}{l}+2\delta-\frac{k^2+l^2}{l}\cdot\frac{r}{l}+\frac{k^2+l^2}{l}\cdot\frac{m'}{m}\frac{s}{l}$$
$$+\frac{i}{ml} \qquad \ldots\ldots \quad (31)$$

neglecting second order terms.

Let T_1 and T_2 denote the nearly equal time periods in the erect and inverted positions respectively.

From (31) we have,

$$\frac{g}{4\pi^2}\mathrm{T}_1^2\, l_1\left(1-\frac{a_1{}^2}{16}\right)^2=\frac{k^2+l_1{}^2}{l_1}-\frac{k^2+l_1{}^2}{l_1}\delta_1+2\delta_1 l_1$$
$$-\frac{k^2+l_1^2}{l_1}\cdot r_1+\frac{k^2+l_1^2}{l_1}\frac{m'}{m}s_1+\frac{i_1}{m} \qquad \ldots\ldots \quad (32)$$

$$\frac{g}{4\pi^2}\mathrm{T}_2^2 . l^2\left(1-\frac{a_2^2}{16}\right)^2 = k^2 + l_2^2 - \frac{k^2 + l_2^2}{l_2}\delta_2 + 2\delta_2 l_2 - \frac{k^2 + l_2^2}{l_2} r_2 + \frac{k^2 + l_2^2}{l_2}\frac{m'}{m} s_2 + \frac{i_2}{m} \qquad \ldots\ldots \quad (33)$$

k^2=square of the radius of gyration about the parallel axis through the C.G. of the pendulum.

$$= l_1 \times l_2 \qquad \ldots\ldots \quad (34)$$

$$\delta_1 = \frac{\alpha . mgl_1}{l_1 + l_2} \qquad \ldots\ldots \quad (35)$$

$$\delta_2 = \frac{\alpha . mgl_2}{l_1 + l_2} \qquad \ldots\ldots \quad (36)$$

From (35) and (36) we get,

$$l_1 \delta_2 = l_2 \delta_1 \qquad \ldots\ldots \quad (37)$$

$$(\delta_1 l_1 - \delta_2 l_2) = \alpha . mg\,(l_1 - l_2) \qquad \ldots\ldots \quad (38)$$

Equations (32) to (38) lead to the following result,

$$\frac{g}{4\pi^2}\left\{\frac{\mathrm{T}_2^2 l_1 \left(1-\frac{a_1^2}{16}\right)^2 - \mathrm{T}_2^2 l_2 \left(1-\frac{a_2^2}{16}\right)^2}{l_1 - l_2}\right\}$$

$$= l_1 + l_2 + \alpha . mg + \frac{l_1 + l_2}{l_1 - l_2}(r_2 - r_1) + \frac{m'}{m}\frac{l_1 + l_2}{l_1 - l_2}(s_1 - s_2) + \frac{i_1 - i_2}{m(l_1 - l_2)}$$

$$= l_1 + l_2 + \alpha . mg + \frac{L}{l_1 - l}(r_2 - r_1) + \frac{m'}{m}\frac{L}{l_1 - l_2}(s_1 - s_2) + \frac{i_1 - i_2}{m(l_1 - l_2)} \qquad \ldots\ldots \quad (39)$$

$= l_1 + l_2 +$ sum of the four individual corrections, thus involving all the four corrections.

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Auto-counter for Fills and Draws of Reaction Vessels and Auto-controller for Distillates

By

GANAPATI NARAYAN GOKHALE

A. AUTO-COUNTER FOR FILLS AND DRAWS OF REACTION VESSELS

THIS instrument gives a better control and increased efficiency in factories using dosing devices, settling tanks, chemical reaction vessels, etc., where the operations of filling and emptying are very frequent.

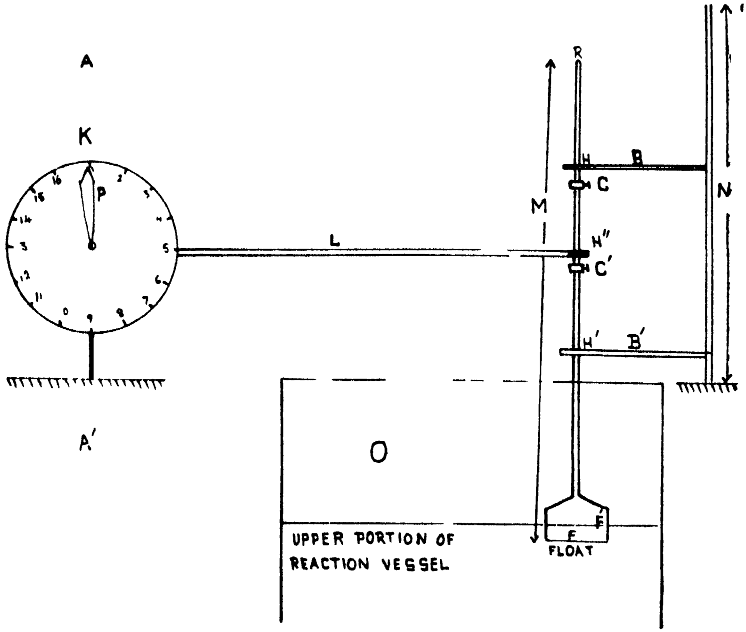


Fig. 1—Section in Plane of Dial of Auto Counter

DESCRIPTION OF THE INSTRUMENT

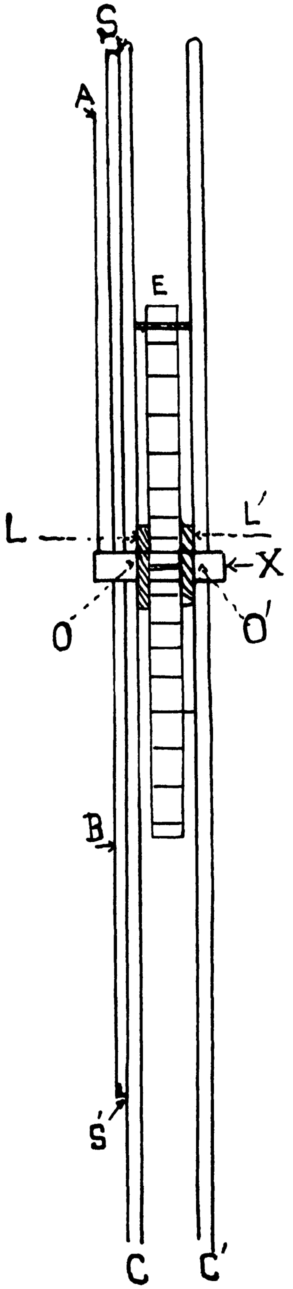


Fig. 2—Section Through AA′ of Figure 1

1. General

A sectional view of the apparatus in plane with the dial is shown in figure 1. K is a counting mechanism with a dial and a pointer P. L is the lever arm. M is the float with brass collars. N is the stand for supporting the float. O is the reaction vessel which is filled and emptied frequently.

2. Counting Mechanism

(*a*) Refer figure 2 : Two flat iron bars C and C′, 1 inch thick, support the mechanism. At a suitable height there are two holes O and O′, through which an axle X passes. To the front bar C are fixed seats S and S′ on which a dial B is screwed up. Required number of marks are painted on the dial. In front of the dial, on the end of the axle, is fixed a pointer A. The dial and the pointer are made of galvanised iron sheets 1/16 inch thick. Inside the supporting bars C and C′, one on each side and just touching them come two lever arms L and L′, 1-inch thick, resting and freely able to move on the axle X. The other ends of the lever arms go towards the float. The lever arms are 1-inch broad and of a suitable length. Between the lever arms comes the cog-wheel E fixed firmly on the axle with a pin.

(*b*) Refer figure 3 : The cog-wheel has as many teeth as the number of counts desired on the meachanism. On one of the supporting bars O is fixed a seat to which are attached a pin D, a stop C and a spring B. This pin allows the cog-wheel to rotate only in one direction. C′, D′ and B′ are stop, pin and spring fixed on the lever arm L.

3. *Float Mechanism*

Refer figure 1 : The float F should be made of glass, iron, copper, aluminium, etc., depending upon the reactivity of the liquid in which it is desired to be used. While floating, portion of the float dipping below the surface of the liquid should not exceed half its height. See line F′. A hollow rod, half an inch in diameter, of any suitable metal, is screwed on the mouth of the float. In order to hold the float vertical, to an iron stand N fixed firmly, are attached 2 flat iron bars B and B′ horizontally at suitable distances, at each end of the bar is kept a hole H H′, through which the float arm R can just pass smoothly. Between the bars B and B′, on to the float arm R are fixed brass collars C and C′. The position of the brass collars C and C′ can be adjusted by means of screws. The outer diameter of the brass collars C and C′ is kept bigger than the diameter of the holes H and H′. Between the 2 lever arms shown by L, is a brass ring H″, firmly fixed on the ends, which can pass smoothly on the float arm R.

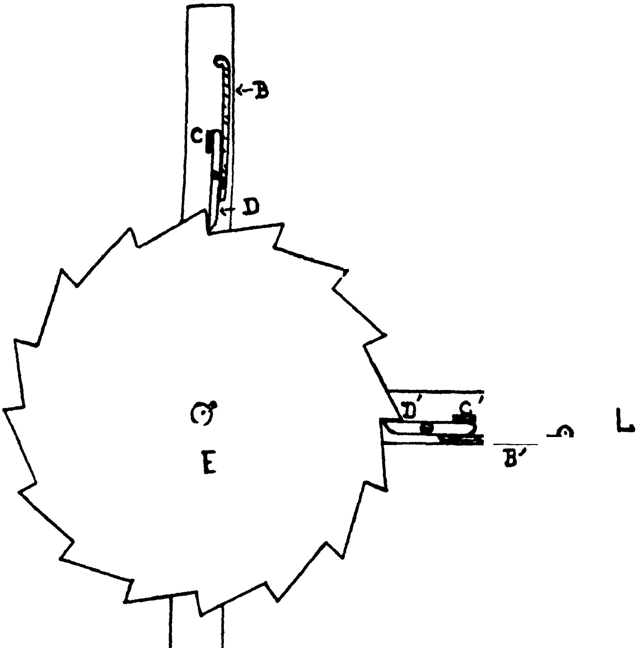


Fig. 3—Section in Plane with the Cogwheel

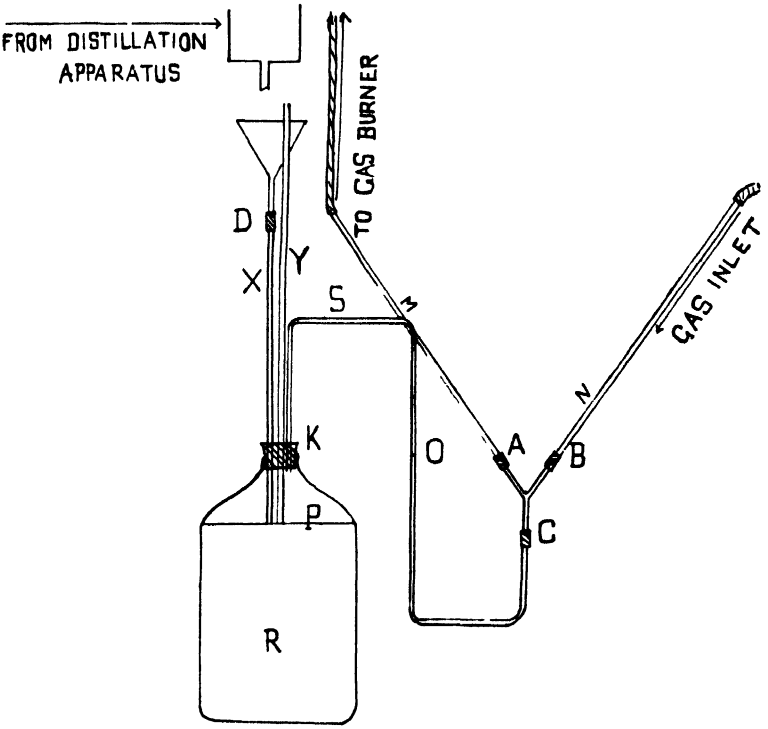
WORKING

Refer figure 1 : As the reaction vessel is filled, the float F resting on the brass collar C′, is gradually lifted. The brass collar C′ then touches H″ and lifts the end of the lever arm L, till the upper brass collar Ctouche Hs.

Refer figure 3 : The pin D′ which is attached to the lever arm L, pushes the cog-wheel up. This makes the pointer to move by one division. During the process of emptying the vessel, the float moves down, till its motion is stopped by the lower brass collar. The pin D′ attached to the lever arm L slides over the tooth of the cog-wheel, while the pin D fixed upon the supporting stand O holds the cog-wheel in position. The angle through which the lever should move can be controlled by adjusting the position of the brass collars C and C′ (figure 1). The angle should be so arranged that at each fill, the cog-wheel will be turned up by one tooth, which will be indicated by the pointer P (figure 1), on the dial.

B. AUTO-CONTROLLER FOR DISTILLATES

THE device invented is of use for collecting definite quantities of distillates in places where gas is used for heating purposes. It is easy to assemble either with glass or metal tubing at a negligible cost. It saves labour, gas and distillates.



DESCRIPTION OF THE APPARATUS

Arrange the apparatus as shown in the figure. The tubing used should have an internal diameter of about 3/16 inch. A, B, C and D are small rubber joints of pressure tubing. Keep funnel tube X and vent tube Y more than double the length of pressure in inches of water, at which gas is supplied to the burners. Keep the funnel below the distillate in such a way that the drops will fall on its sides. The lower end of the vent tube should be in level at which the distillation is required to be stopped. The lengths of the tubes M and N should be more than 8 inches.

WORKING

Fix rubber bung K tightly. Disconnect rubber tubings at joining A and B. Pour water in the Y-shaped tube till it overflows. It will enter the tube S upto the point O. Put pressure tubings A and B. Turn the gas on. The gas will push the water from the arms of the Y-shaped tube, down below the elbow and the burners will burn when lighted. When distillate will reach the line P in the receiving vessel for distillates, it will block the lower end of the vent tube Y. Water will rise in the funnel and vent tubes. The pressure will force the water from the elbow of the Y-shaped tube up into the arm M. This will block the passage of gas and the burners will be extinguished. This stops ultimately the distillation.

MUNICIPAL LABORATORY,
BOMBAY

[*Received : July 16, 1942*]

ABSTRACTS OF M.Sc. THESES

I—Studies in Aqueous Solutions of Aluminium Oxide in Alkali Hydroxides

By

V. T. Sheth

EQUILIBRIUM concentrations of solutions obtained by shaking aluminium hydroxide with solutions of the hydroxides of sodium and potassium were studied. For this purpose, four different samples of aluminium hydroxide were used : (*i*) obtained by precipitation from aluminium sulphate, (*ii*) Merck's sample as obtained from the manufacturers, (*iii*) obtained by precipitation from aluminium chloride and (*iv*) obtained by the hydrolysis of aluminium ethoxide. The concentration of the alkali was varied between 1N and 14N and the temperature range was from 35° and 55°C. The results show that the solubility follows the order given above for the different samples, being greatest for the sample obtained from aluminium sulphate and least for that obtained from aluminium ethoxide. It is also found that the solubility of each sample increases with th concentration of the alkali as well as with increase in temperature. The amount of alumina precipitated by the addition of an electrolyte has been determined in each case and it is noticed that the amount of alumina thus precipitated is in the reverse order of solubility, *i.e.*, largest amount is precipitated from the sample obtained from aluminium ethoxide whereas the least amount is obtained from the sample obtained from aluminium sulphate.

II—Some Attempts to Make out the Mechanism of Chemical Reactions : Studies in Chemisorption of Oxygen on Charcoal

By

B. K. Trivedi,

M. R. Sc. Institute, Gujarat College, Ahmedabad

IN continuation of the work on the combustion of charcoal in oxygen, nitric oxide and nitrous oxide (Shah, J., 1929, pp. 2661-2692) and on the heats of absorption of gases on charcoal (Sharangpani, M Sc. thesis—1935) attempts have been made (in the present work) to elucidate the nature of chemisorption of oxygen and oxides of nitrogen on charcoal.

Series of quantitative experiments have been conducted with sugar charcoal exhausted at 900° and (A) oxygen, (B) nitric oxide and (C) nitrogen tetroxide at various temperatures between 0° and 300°. At each temperature, the charcoal containing chemisorbed oxygen with or without retained oxides of nitrogen in vacuo has been examined by (*i*) 'heat treatment' in successive stages upto 900° (Shah, *loc. cit.*), and (*ii*) 'water treatment' first with ice cold water and then with hot water (King, J., 1933, p. 842). The analysis of the gas evolved in (*i*) revealed the extent of chemisorption of oxygen and retention of oxides of nitrogen on charcoal in vacuo at different temperatures and that of the cold and hot aqueous extracts in (*ii*) showed the amounts of chemisorbed oxygen and retained oxides of nitrogen giving rise to oxalic acid and nitrous and nitric acids respectively.

The results, on the whole, show that the state of chemisorbed oxygen on charcoal is affected by a rise in temperature, treatment with water and when surrounded by (*i*) oxygen, (*ii*) nitric oxide, and (*iii*) nitrogen tetroxide. The retained nitric oxide in experiments with nitric oxide is *neither* chemisorbed like oxygen *nor* is under the influence of chemisorbed oxygen on charcoal but exists as condensed N_2O_4 or N_2O_3, *i.e.*, along with nitric oxide in the absorbed state on charcoal, an observation confirmed from the behaviour of charcoal towards nitrogen tetroxide. In the interaction between charcoal and nitric oxide at low temperature the charcoal surface starts and catalyses the auto-oxidation of nitric oxide, *i.e.*, the formation of nitrogen tetroxide with the liberation of nitrogen, and the nitrogen tetroxide so formed then interacts with charcoal leading to the chemisorption of oxygen and production of carbon dioxide and nitrogen through the chemisorbed oxygen, the behaviour of charcoal with the chemisorbed oxygen and retained oxides of nitrogen in vacuo derived from both the nitric oxide and nitrogen tetroxide experiments being of the same type in 'heat treatment' and 'water treatment,' except in the sense that the chemisorption of oxygen and retention of nitrogen tetroxide proceeds more pronouncedly in the nitrogen tetroxide experiments than in the nitric oxide experiments.

M. S. S.

NOTES AND NEWS

A Lesson From a Living Organism

A STUDY of a healthy living organism shows that there are two important processes at work in its mechanism. These processes apparently seem to be contradictory to each other, but are really two aspects of a larger process which may be defined as one of organization. Every organic body or living organism exemplifies these two processes at work within itself—of insulation or specialization on the one hand and unification and synthesis on the other.

The first process shows a disintegrating and the second an integrating tendency. An organ in an organic body fulfils its appointed function only when it specializes in that function. The greater the specialization of the organ, the more clearly it will be differentiated from the other organs and the richer will be its contribution to the life of the whole organism when it co-operates and is co-ordinated with the other organs.

In the perfect organism each side of the process will be more definite and outstanding, namely, specialization and synthesis. This holds true not only in the case of a simple physical organism, such as the human body, but also in those of larger and more complex organisms on the plane of feeling and thought, or on the cultural plane, which might result from the grouping together of human beings having some common ideals as their objective. The grouping may be of a learned society, a literary, scientific or art society, or it may be a grouping of persons with common cultural or religious ideals. These groupings of persons may again be small as those of learned societies or large as those of religions, nations, civilizations, etc.

Whatever the organism or the organization may be, the same two processes, one of isolation and specialization and the other of synthesis and unification are always at work ; the latter process is sometimes not so evident as the former but it is there all the same and requires some insight to be noted and emphasized.

With this knowledge of the scientific laws of the building and growth of an organism in the background, let us look at the process of the organization of the Indian nation which is taking place before our eyes. We shall now be in a position to understand more clearly the apparently hopeless and paradoxical situation in which we find our mother-country placed to-day.

The idea of "Pakistan" which is in the air now must be taken to mean the first process at work on the *cultural* level. The idea of "Pakistan" applying it to any body of persons, Muslims, Jains, Sikhs, etc., on the *physical* plane is unscientific; but on the plane of feeling and thought it has got a definite meaning. This means that each community, Muslim, Hindu, Sikh, Jain, Christian, Parsi, Jew, etc., etc., has to specialize in its own unique traditions, its peculiar social, religious and racial culture. No government should interfere with the cultural growth of any community but on the other hand give every possible facility and encouragement to take the cultural development to the highest possible pitch. This will be in perfect conformity with the biological laws of growth.

But just as an organ, for example, liver or heart, however specialized it may be, cannot live alone but has to co-operate with the other organs of the body to subserve the life of the whole organism, similarly, the different communities of individuals, however cultured they may be ard howsoever much specialized in their peculiar traditions and unique racial characteristics, cannot live alone or become isolated on the physical plane, for that would mean not only their death but also the death of the whole organism, but should co-operate with one another to subserve and sustain the life of the mother organism. Only thus will a living Indian nation, which is in the process of forming, come into existence. And the Indian nation will be all the stronger and richer by the fact of the cultural development of her different daughter communities and she will be all the more vitalized by their co-operation with one another for a common ideal.

Each separate community must be free to work out its own destiny in its own way and to develop to the highest point possible its own individuality but its watchword should be in relation to the other sister communities and the motherland "*together differently*." Each will bring its own special contribution to the unified richness and variety of the larger life of the mother-organism.

The Indian nation has, again, to make its own unique contribution to the world culture in co-operation with the other nations with their unique cultures. This is possible only when each nation is free to grow along its own line of growth. In a truly organic internationalism both the freedom of each individual nation and the mutual interdependence of each should not be forgotten.

What a fine place of abode this earth of ours would be to live in if the leaders of each faith and community and the rulers of each state and nation understood these simple biological laws of growth and applied them to the building of a great nation like India or a great world organization which would serve as the cradle of a new civilization broad-based on the natural laws of the growth of a living organism!

D. D. KANGA

OBITUARY

Sir William Henry Bragg, O.M., F.R.S.

THE scientific world has lost one of its most distinguished leaders in the death of Sir W. H. Bragg, Director of the Royal Institution, London, on the 12th March, 1942, at the venerable age of nearly 80 years. Even a bare recollection of Sir William's glorious life is enough to impress the mind with wonder and admiration. Born in 1862, he graduated from Cambridge and went overseas at the age of twenty four to take up the Professorship at the Adelaide University. He published his first paper in 1904 and this marked the beginning of a series of brilliant contributions made by him to scientific knowledge, and won for him the Fellowship of the Royal Society in 1906. In 1909, he was appointed Professor of Physics at the University of Leeds, and in 1915. Quain Professor of Physics at the University College, London. In 1923, he was appointed Director of the Royal Institution, which position he held till his death.

Bragg's early work was carried out on radioactivity. He studied the ionisation of gases by the passage of alpha particles through them, and showed for the first time that it falls off abruptly after they traverse a certain distance (Range) in a medium.

Sir William's most important work, for which he is primarily known, is on X-rays and Crystals. The question of the nature of X-rays engaged his attention for a long time and at one time he considered them as streams of neutral particles. But when Laue showed in 1912 that X-rays are electromagnetic waves and can be diffracted by crystals, Bragg took up the study from the new view point and in the same year developed theoretical considerations for the interaction of X-rays with crystals and derived the expression generally known as Bragg's Law. He designed an X-ray Spectrometer, which he first employed for the study of crystals of rock salt and sylvine, and in collaboration with his son, now Sir Lawrence Bragg, who had taken a special course in crystallography, discovered a new method for determining the wave-length of X-rays and unravelled at the same time the structure of the two crystals. Sir William and his son concentrated their attention on the study of crystals to discover the mysteries of Nature in building up crystalline structures of substances which belong to both the inorganic and organic worlds.

Sir William's fame spread far and wide and a large number of workers were attracted to Davy-Faraday Laboratory from all parts of the world.

The writer came in contact with him on two occasions when he went to work in the Laboratory in 1926 and 1934. On both occasions he found him deeply interested in organic crystals. He took personal interest in all the workers and encouraged them to develop new lines of investigation and carry them to perfection.

Sir William's technical, or rather "applied," work was mostly done on account of the exigencies of the war. It dealt chiefly with the transmission and detection of sound under water, and included investigations on the directional properties of vibrating circular membranes, the invention of the 'Button Hydrophone' and the 'Amplitude Meter.' A popular account of this work is given in his book *World of Sound.*

It is no exaggeration to say that in his mastery over exposition Sir William Bragg was excelled by few. He was one of the most popular lecturers on scientific subjects. His lectures, which were always well attended, had nothing of the terseness of the scholar nor anything of the scholasticism of the school master. They were delivered in simple style and made interesting by a happy analogy or an experimental set-up, startling in its simplicity.

Sir William Bragg was well honoured in his country and abroad. He was awarded the Nobel Prize in 1915, jointly with his son, W. L. Bragg, and was the recipient of Copley Medal and several others. He received the honour of Knighthood in 1920 and later on the distinction of Order of Merit. He was the President of the Royal Society and a distinguished Honorary Fellow of several Foreign Societies.

Sir William Bragg was an enthusiastic worker and even a few months before his death took an active interest in the discussion held at the Royal Society on the "Extra Spots in Laue Photographs" and contributed a few papers to this discussion. He was a great writer and besides "X-rays and Crystal Structure," "An Introduction to Crystal Analysis" and "Crystalline State," he also published a series of popular books which will delight their readers for many years to come. He was keenly interested in the social relations of science, and only a short while before his death he contributed an article on "Science and the Community" to the first issue (January, 1942) of *Endeavour*, a quarterly review published by the Imperial Chemical Industries, London.

MATA PRASAD

BOOK REVIEW

Differential Equations.—By G. S. Diwan and D. S. Agashe (Published by D. S. Agashe). n. p.

THE work under review is a text-book on elementary differential equations, intended for a first degree course in many Indian Universities, in which for years Murray's text-book was used and later on Piaggio's book appeared as a suitable alternative. On the whole the work under review is well suited for the purpose. Differences of opinion must exist on the method of presentation of various subjects and on the sequence followed. For example, the solution of the standard linear differential equation of the first order is made to depend (in § 19) on the Rule III of Integrating Factors. In certain courses of studies of Indian Universities the subject of integrating factors (§§ 11, 13-17) is omitted from the syllabus, and hence a direct method of solving this equation should have been given, at least as an alternative. Certain nomenclatures and definitions are also unusual. For example, on P. 9, c_1 and c_2 are called *mutually dependent* constants. The meaning is made clear only on P. 10, where constants which are not independent (as defined) are defined as dependent constants.

There are some obvious slips. For example, on P. 9 in the foot-note†, the statement is seen to be wrong if we take *two* functions $c_1+c_2+c_3$ and $(c_1+c_2+c_3)^2$ of *three* arbitrary constants and replace them by *distinct* constants c' and c'' respectively; on P. 11, the constants λ_1, λ_2, λ_3, λ_4 in $\lambda_1 y^2+\lambda_2 y+\lambda_3 x+\lambda_4=10$ are not independent; on P. 14, a certain result is referred to as 'an assumption' in line 12 from the bottom, but it is not called an assumption, as should have been done for clarity, in the first line on that page; on P. 23, 'Conversely' would have been more appropriate in line 3 than 'Further'; on P. 60 in line 16 from the bottom, the factor is $p-f_r$, not $p-f_r=0$, and so on.

On P. 41, it would have been better if the theorem proved in § 11 had been enunciated first and a definition of 'independent' functions given, if at all this result was to be given the status of a theorem, as seems to be the authors' intention. On P. 62, in § 3, it is not clear as to what is meant by 'Let us assume........................in Chapter II.' From the foot-note on P. 62 one would think the assumption to be that the extraneous factors (not containing $\frac{dp}{dr}$) should be rejected, as in Ex. (1) in § 3.2. Even if that is done, it is possible that the equation left may not be solvable by any of the methods described in Chapter II. I would have preferred stating clearly 'If this equation......can be solved by any of the methods described in Chapter II.'

I have not the necessary space to make my lists exhaustive. The book is fairly well-written and the printing is carefully done, except that the breaking up of equations and spreading them over two lines could have been avoided in many places. In spite of minor blemishes, some of which are pointed out above (in the hope that when the second edition is published, they may be removed), the book is a welcome addition to Indian publications on the subject.

N. M. S.

LIST OF THESES

Table showing M. Sc., Ph. D. and D.Sc. theses in Mathematics, Physics, Chemistry and Geology (from October 1941 to September 30, 1942)

Name of the Candidate	Subject of the Thesis	Name of the Professor under whom the candidate worked	Name of the Institution
	M.Sc.		
	Physics		
Akber, G. H.	Study of the Excitation of a Band System from a Metal and its Oxide	Dr. N. R. Tawde	R.I.Sc.
Belani. J. D.	Distributions of Scattered X-Rays	Dr. S. G. Khubchandani	D.J.S.
Gadre, K. L.	Measurement of the total precipitable water in the atmosphere above Poona by measurements of absorption in the near Infrared	Dr. L. A. Ramdas	I.M.D
Gokhale, S. V.	The Ionic Diamagnetic Susceptibilities of $\mathrm{Ca}^{\cdot\cdot}$ and $\mathrm{Sr}^{\cdot\cdot}$ in Heteropolar Solid Salts of Inorganic and Organic Acids	Principal G. R Paranjpe	R.I.Sc.
Pandya. N. S.	Studies in Raman Spectra	Professors M. D. Avasare and D.V. Gogate	B.C.
Unvala, H. A.	Direct Measurements of Spectral Intensity Distributions	Dr. N. R. Tawde	R.I.Sc.
	Chemistry		
Airan, J. W.	1. Action of sulphur monochloride, sulphur dichloride, thionyl chloride, and sulphuryl chloride on Naphthol derivatives. 2. Study of the oil from the seeds of Staranise (Badam ful)	Dr. S. V. Shah	R C.
Bavadekar, V K.	1. Condensation of butyl ether of phenol with acetone dicarboxylic acid. 2. Reaction of β-2:4-dimethoxy-Phenyl glutaconic acid. 3. Action of sodium acetate and acetic anhydride on the anhydrides of β-(2 : 4-dimethoxy-phenyl) and β-(4-butoxy-phenyl) glutaconic acids). 4. Syntheses of 2-benzoyl-4-butyl-resorcin and 4-methyl-4′-phenyl-6-butyl-coumorin-7:8-α-pyrone	Professor D. B. Limaye	R.I.E.I.

Name of the Candidate	Subject of the Thesis	Name of the Professor under whom the candidate worked	Name of the Institution
Bhanage, S. S.	Effect of Hydrogen Ion Concentration on the Time of Setting of Various Inorganic Gels	Dr. Mata Prasad	R I Sc.
Chandrasekharan T. R.	Studies in the Isomerism of Cyclohexane Derivatives	Professor R N. Bhagwat (Prof. V. V. Nadkarni)	
Dordi, J. B.	Activation of Charcoal by Group II Metal Chlorides	Professor V. V. Nadkarni	St. X.
Fenani, V. G.	Thermal decomposition of calcium sulphate in the presence of boric oxide and its mixtures with other metallic oxides	Professor S. M. Mehta	R.I.Sc.
Guruswamy, S.	Studies during gelation and coagulation	Dr. Mata Prasad	R.I.Sc.
Kanekar, C. R.	Magnetic Properties of Barium Ion and its Compounds	Dr. Mata Prasad	R.I.Sc.
Kotwani, N. G.	Studies in Coumarins	Professors J. V. Lakhani and G. D. Advani	D.J.S.
Kulkarni, R. N.	Benzylidene Flavones Considered as Chalkones	Dr. R. C. Shah	R.I.Sc.
Kurlekar, M. V.	1. Synthesis of 4:4′ diphenylcoumarin-6:7-α-pyrone. 2 Synthesis of 7-hydroxy-2 prophyl-3 butyryl-chromone and observation of the influence of the "butyryl" group in the 3″ position in the 7 hydroxy-2-propyl-3 butyryl-chromone on Frios Migration. 3. Synthesis of propyl-2′ methyl-3′ acetylchromone-7:8-α-pyrone. 4. Synthesis of 2-butyryl-4-ethyl resorcin by the extension of the Nidhone process for the synthesis of 2-Acyl-resorcins.	Professor D. B. Limaye	R.I.E.I.
Mappara, R. K.	A study in the reactivity of the Hydrogen atom of the (-NH) group situated between two keto groups	Professor L. D. Shah	M.T.B.
Mehta, M.D.	Activated carbon from waste raw materials	Professor R. N. Bhagvat (Prof. V. V. Nadkarni)	St. X.
Mehta, S. D.	The Time of Setting of Nickel Hydroxide Gels in the Presence of Electrolytes and Oppositely Charged Sols	Dr. Mata Prasad	R.I.Sc.

Name of the Candidate	Subject of the Thesis	Name of the Professor under whom the candidate worked	Name of the Institution
Mehta, S. H.	1. Synthesis of 2-benzoyl-4-ethyl-resorcin by the Nidhone process for the synthesis of 2-acyl-resorcins. 2. Studies of 8-benzoyl-6-ethyl-4-methyl-umbeliferone. 3. Studies on 2 benzoyl-4-ethyl resorcin	Professor D. B. Limaye	R.I.E.I.
Padwal, N. A.	Opacity Measurements during Gelation and Coagulation	Dr. Mata Prasad	R.I.Sc.
Parekh, N. B.	Studies in Coumarins	Dr. R. C. Shah	R.I.Sc.
Rawtani, A. S.	The Parachor and Chemical Constitution: (1) Determination of parachor values of some elements from the surface tension measurements of aqueous and non-aqueous solutions of their simple salts; (2) Determination of structure of some complex and double salts from their parachor values	Dr. J. V. Lakhani	D.J. S.
Sant, U. A.	1. Kinetics of the decomposition of potassium chlorate heated in the presence of oxides and salts of Titanium Vanadium, Chromium, Iron, Cobalt, Nickel and Copper. 2. Catalytic decomposition of bleaching liquor in presence of the salts of Nickel, Cobalt and Copper. 3. Kinetics of the reduction of a solution of potassium chlorate by an acidified solution of sulphur dioxide. 4. Study of the Hydrolysis of Chlorine	Professor G. B. Kolhatkar	F.C.
Sathe, S. V.	1. Dielectric Constants of some Inorganic Salts, 2. Dipole Moments of Glyptals	Professor B. V. Bhide	Sir P.
Sheth, V. T.	Studies in aqueous solutions of aluminium oxide in alkali hydroxides	Professor S. M. Mehta	R.I.Sc.
Shiralkar, N. K.	1. The effect of butylation on the course of hydrolysis of 7-hydroxy-4-methyl-coumarin, and 7-hydroxy-8-acetyl-4-methyl-coumarin with caustic alkali. 2- Synthesis of 2 butyril-for-butyl-resorcin by the extension of the nidhone process for the production of 2-acyl-resorcins	Professor D. B. Limaye	R.I.E.I.

Name of the Candidate	Subject of the Thesis	Name of the Professor under whom the candidate worked	Name of the Institution
Trivedi, B. K.	Some attempts to make out the mechanism of chemical reactions: Studies in chemisorption of oxygen on charcoal	Professor M. S. Shah	G.C.
Trivedi, P. L.	Studies in Kostanecki-Robinson Reaction	Dr R. C. Shah	R.I.Sc.
Walvekar, S. P.	Mechanism of the Fission of Aromatic Ethers by Halogen Acids in Different Solvents	Professor B. V. Bhide	Sir P.
	Geology		
Ogale, B. Y.	A Study of Rocks occurring near Bilgi in Bijapur District	Professor K. V. Kelkar	F. C.
	Ph.D.		
	Mathematics		
Sen, D. K.	1. Interpolation and Summation Formulas and properties of Factorials. 2. Numerical Solutions of Equations with one unknown. 3. Motion of sphere and ellipsoid in a viscous liquid	Independent Work	
	Physics		
Karve, C. S.	1. Development of a new visibility meter and its comparison with other visibility meters in the laboratory and under open air conditions. 2. Diural variation of visibility of objects at different altitudes and in different directions. 3. Evaporation from moist spherical surfaces and its application to problems of psychrometry, formation and dissipation of fog, etc.	Dr. K. R. Ramanathan	
	Chemistry		
Bhave, V. M.	1. Condensation of Acetone-dicarboxilic Acid with Resorcinol Dimethyl-ether; 2. Condensation of Salicyl-aldehyde with Esters of β-aryl Glutaconic Acids; 3. Condensation of Acetone-dicarboxylic Acid with Thymolmethyl-ether; 4. Condensation of the Anhydrides of βaryl Glutaconic Acids with Phenol Ethers	Professor D. B. Limaye	R.I.E.I.

Name of the Candidate	Subject of the Thesis	Name of the Professor under whom the candidate worked	Name of the Institution
Blude, N. V.	1. Comparative Disintegration of the constitutuents of some food grains. 2. Studies in Enzymes during the period of germination	Dr. D. L. Sahasrabuddhe	N.W.C.
Joseph, Olive (Miss)	Studies in Aqueous Solutions of Alkali Aluminates	Dr. Mata Prasad	R.I.Sc.
Kantak, K. V. (Miss)	Physico-Chemical Studies on Mixtures of Boric Acid and Hydroxy Substances	Professor S. M. Mehta	R.I.Sc.
Leley, V. K.	The Phosphate Supplying Power of Soils	Dr. D. L. Sahasrabuddhe	N.W.C.
Mavani, C. K.	Synthetical Experiments in Coumarins and Chromones	Dr. R. D. Desai	St. X.
Radha, K. S. (Miss)	Studies in Polyhydroxy-aldehydo Benzoic Acids	Dr. R. C. Shah	R.I.Sc.
Ranganathan, V.	1. Physico-Chemical Methods for the determination of enzyme activities and substrace concentrations. Estimation of physiologically active components in biological materials. 2 Studies in proteins. The non-protein nitrogen constituents of Indian Food-stuffs. The digestibilities and biological values of the proteins of Indian Foodstuffs 3. Studies in Indian Timbers	Professor V. Subrahmanyan	I.I.Sc.
Virkar, V. V.	Studies in Chromone Series	Dr. R. C. Shah	R.I.Sc.
Waravdekar, V. S.	Studies in Hydroxy arylalkyl-Ketones containing long chain Alkyl radicals	Dr. R. D. Desai	St. X.
	Technology		
Mehta, V. S.	Halogenation of Fatty Acids	Dr. T. N. Mehta	U.D.C.T
Taraporewala, S. I.	Some Aspects of Detergency	Professor K. Venkataraman	U.D.C.T.
	D.Sc.		
Pithawalla, M.B.	A Geographical Analysis of the Lower Indus Basin (Sind) with special reference to the History and Progress of Human Settlements in the Region	Independent Work	

BOOKS RECEIVED

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Acknowledgments

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Bulletin of the Indian Industrial Research
Bulletin of the Indian Lac Research Institute
Ceylon Journal of Science—Section A
D. J. Sind College Miscellany of the Faculty of Science
Endeavour
Hindustan Aircraft Gazette
Indian Aviation
Indian Journal of Physics
International Export Chemist
Journal of the Film Industry
Royal Institute of Science Magazine
The Chemist Analyst
Transactions of the Institute of Marine Engineers
Victoria Jubilee Technical Institute Magazine

JOURNAL OF THE UNIVERSITY OF BOMBAY

NOVEMBER 1942

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EXTERNAL STRUCTURES OF THE DESERT LOCUST

(*Schistocerca gregaria*, Forsk)

(WITH TEXT-FIGURES 53—105)

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By

K. R. KARANDIKAR, B.A., M.SC., PH.D.,
Biology Department, Elphinstone College, Bombay

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INTRODUCTION

THIS part of the external anatomy of the *desert locust* was partly worked out in the Entomology Laboratory of the University of Edinburgh, during the writer's stay in Great Britain, in the winter of 1930-1931. After a lapse of some ten years, the work was again taken up in the summer of 1941, when living material of the locust was made available through the kindness of Mr. T. R. Tulyani of D. J. Sind College, Karachi, to whom the writer is much obliged. With the help of this material, the embryonic and post-embryonic development of the abdominal structures of the locust was exhaustively studied in the Zoological Laboratory of the Royal Institute of Science, Bombay. Sincere thanks are due to Prof. P. R. Awati of the Institute *for giving the necessary facilities for this study in his laboratory.*

The problem dealing with the number of abdominal segments of insects has, for a long time, been a point of much controversy. Differences in numbering these segments have led to a good deal of confusion among entomologists. Various theories have been advanced, many of which have been fully discussed by Newell (1918). Heymons (1896) propounded the theory of a 12-segmented abdomen in primitive insects. Chopard (1920) supports that view, though he does not clearly explain the developmental fate of the 11th segment. Wheeler (1893) and other investigators hold the view of an 11-segmented abdomen, while Crampton (1929) is of opinion that the insect abdomen is formed of 10 segments only.

Another point of dispute relates to the development and homology of the male and female genitalia of insects. In the case of the female genitalia, for instance, three different views have been held, which are summarised by Imms (1931) as follows :—

(1) Genitalia as specially developed organs (Heymons).

(2) Genitalia as representing the embryonic appendages of the 8th, 9th and 10th abdominal segments (Wheeler).

(3) Genitalia as representing the embryonic appendages of the 8th and 9th segments, those of the 9th having undergone a secondary division into two pairs (Walker, Nel, Crampton).

Irrespective of whichever of these theories may prove to be correct, one fact stands out clearly, that the evidence on which they are based is derived almost entirely from a study of the comparative morphology of the adult, without any direct reference to the embryological background of the insects dealt with. In the words of Imms (1931) "the majority of contributions deal with completed organs. Ontogenetic studies have not been pursued with the same enthusiasm."

The diversity of views regarding the number of abdominal segments and the homologies of the genitalia is due to the fact that the terminal abdominal segments of insects usually undergo a radical modification in structure in the course of their embryonic development. This consequently makes it extremely difficult to follow their morphological relationships in the completed organs of the adult. To establish the correct structural homologies, one has therefore to study the insect right from the embryonic stage to the adult condition. With this end in view, the writer has carried out the ontogenetic study of the abdominal segments and the genitalia of the *desert locust,* the results of which are incorporated in this paper.

PROXIMAL ABDOMINAL REGION

The number of abdominal segments visible in *S. gregaria* is eleven of which the proximal eight are clearly seen, while the remaining ones at the distal end are slightly attenuated and modified to form the genitalia, particularly on the ventral side. Each abdominal segment consists of a chitinous dorsal half-ring called the *tergite*. (Fig. 53.T), a chitinous ventral half-ring, the *sternite* (Fig. 54.S), and a narrow membranous area stretching laterally between them on each side. The lateral margins of the tergite are slightly folded inwards to form on each side a narrow chitinous strip called the *sub-tergite* (Crampton, 1925). The latter bears a small *spiracular opening* (SP) near its anterior end and such paired spiracles are present on the subtergites of the proximal eight abdominal segments. The different segments of the abdomen are connected with one another by means of the intersegmental membranes which normally lie concealed under the overlapping posterior margins of the tergites and the sternites.

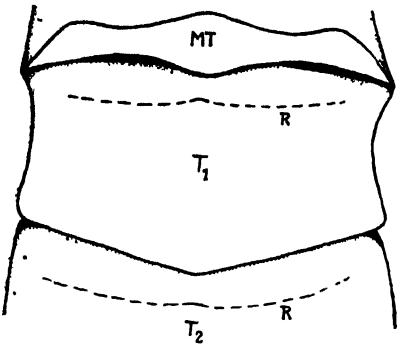

Fig. 53. First abdominal *tergite*. ×6.

MT—Metanotum. R—Ridge (internal). T_1, T_2—First and second abdominal tergites.

The first abdominal *tergite* (Fig. 53.T) is connected with the postnotal plate of the metatergum (MT) by means of a suture which internally gives rise to a strong ridge, and a pair of vertically hanging apodemes. Laterally the tergite carries the tympanic cavity containing the *tympanum* (Fig. 52.TM), serving for auditory purposes. In front of the tympanic cavity is situated the first abdominal *spiracle* (SP) on each side. The first abdominal *sternite* (Fig. 54.S1) migrates forward into the metasternal region, and thus occupies the area between the metathoracic coxae (CX3). It has a narrow median process directed anteriorly and "dovetailed" between the lateral sclerites of the metasternum (MS3). The pleural region of the first abdominal segment is almost crowded out by the excessive development of the basal region of the hind coxae (Fig. 52).

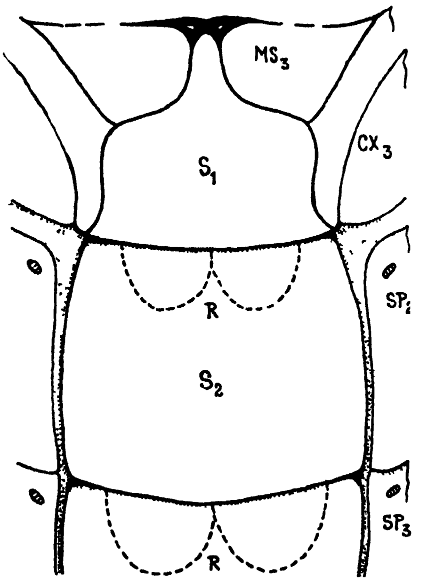

Fig. 54. First and second abdominal *sternites*. ×6.

CX_3—Third coxa. MS_3—Metasternal lobe. R—Ridge (internal). S_1, S_2—First and second abdominal sternites. SP_2, SP_3—Second and third abdominal spiracles.

The proximal abdominal tergites carry on their inner surfaces a deeply chitinised *transverse ridge* on each, running almost parallel to, and situated a little behind the anterior margin of each tergite (Fig. 53.R). These ridges are incomplete laterally and serve in general for muscle attachment. They become rather obscure in the distal abdominal tergites. Similar internal ridges, somewhat of a semicircular shape, are also present on the inner surfaces of the sternites of the 2nd, 3rd, 4th and 5th segments, serving likewise for muscle-attachment (Fig. 54.R). Besides these, the abdominal sternites are provided with internal *apophyses* serving the same purpose. Each sternite possesses generally two pairs of them, arising from its antero-lateral corners, one pair being directed anteriorly in the horizontal plane, and the other dorsalwards in the vertical plane. The first abdominal sternite carries no such internal apophyses ; the second has only the anteriorly running pair ; while the third and the succeeding five sternites possess the two typical pairs of apophyses on each of them. The ninth sternite of the male has only one pair of flattened apophyses occupying the latero-vertical position. The ninth sternite of the female has also a single pair of apophyses which, unlike the preceding ones, are very long and blade-like and project cephalad in the body-cavity.

DISTAL ABDOMINAL REGION

The foregoing description refers to the proximal abdominal segments of *S. gregaria*, and applies equally to both the sexes of the locust. The distal abdominal segments of this insect show however a definite tendency to reduction in size and modification in structure, due to their being closely associated with the development of the external genitalia. This distal segmental shortening, coupled with structural modifications, has caused a good deal of confusion, not only in numbering the abdominal segments, but also in respect of the homologies of the genital structures. To clear up this confusion and arrive at a correct interpretation of the genitalia, it is essential to study the embryonic development of the distal abdominal structures before they attain the status of completed organs in the adult stage.

EMBRYONIC DEVELOPMENT OF THE ABDOMINAL STRUCTURES

A microscopic examination of the ventral side of the embryo of *S. gregaria*, in its very early stage, shows the abdomen to be clearly formed of eleven segments (Fig. 55). Each segment is composed of a median *sternal plate* (S) which bears laterally a pair of bilobed *appendages*. Beneath the transparent sternal plates are seen the eleven pairs of *nerve ganglia*, corresponding to the eleven abdominal segments. The proximal lobe of each segmental appendage represents, according to Crampton (1929), the Crustacean *protopodite* (PR), while the distal one is homologous with the Crustacean *exopodite* (EX). The Crusracean endopodite is not properly differentiated in the proximal abdominal appendages, except in the case of the first segment, where it, in conjunction with the other parts, gives rise to an ear-shaped glandular structure called the *pleuropod*. The latter persists through the embryonic life and is cast off only at the time of the intermediate moult. As the embryo advances in development, the *protopodites* of the first nine abdominal appendages flatten out laterally and form the sides of the respective sternal plates with which they get indistinguishably fused. The *exopodites* of the proximal eight appendages bear each a small invagination near the anterior margin, which represents the *spiracular opening* (SP). As development proceeds, the exopodites grow in a latero-dorsal direction, become closely associated with the tergal plates (wide infra), and eventually form the so-called *subtergites*. In the distal region of the abdomen, the segmental appendages together with their sternites undergo a modification of their structure, in connection with the development of the genitalia, the details of which are given below.

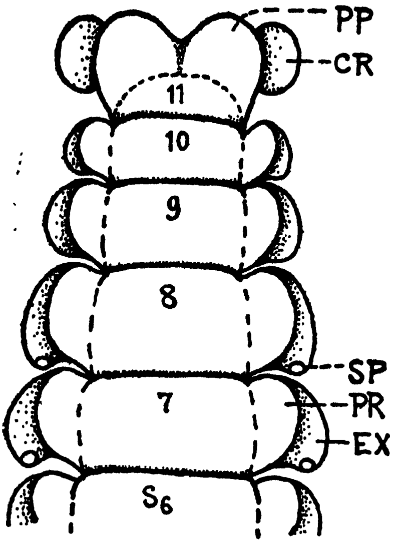

FIG. 55. An early stage *embryo* : Ventral view of the distal abdominal region. ×75.

CR—Cercus. EX—Exopodite. PP—Paraprocts. PR—Protopodite. S_{6-11} —Segmental sternites. SP—Spiracle.

Whatever the fate of the abdominal appendages, their segmental appearance in the early stage of the embryo is by itself a sufficient proof of the *affinity* of insects with Crustaceans. Moreover, the presence of the *eleven* pairs of these appendages and of the eleven pairs of nerve-ganglia, observable very clearly in the abdominal region of the early stage embryo of *S. gregaria*, constitutes an unmistakable evidence in favour of the theory of the 11-segmented abdomen of insects. It may be mentioned here that Roonwal's work (1937) on Locusta migratoria, describing the presence of the eleven pairs of coelomic sacs corresponding to the 11 pairs of abdominal appendages, points to the same conclusion.

Dorsally, the first ten abdominal tergites are represented, in the early stage of the embryo, by the ten pairs of segmentally arranged lateral plates (*tergal plates*) (Fig. 56.L) whose appearance is almost synchronous with that of the bilobed sternal appendages. Between the plates is stored the orange-coloured *yolk* (K) which constitutes the food of the embryo. As development goes on, the margins of these tergal plates, ten on each side, extend gradually upwards in the dorso-mesal direction (Fig. 57) and eventually meet in the mid-dorsal line, thus forming the completed tergites of the first ten abdominal segments. The eleventh tergite, unlike the rest, develops very early as a single terminal piece in the form of a small subovate tergal plate (T11), and is homologous with the so-called *supra-anal plate* of the adult.

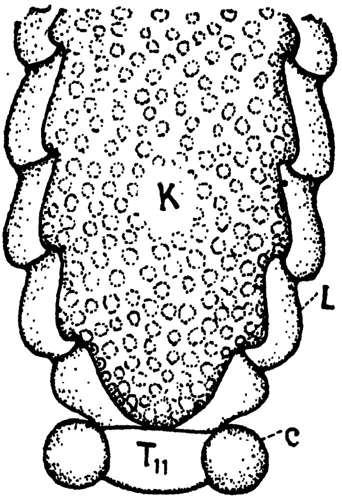

FIG. 56. An early stage *embryo*: Dorsal view. ×75.

C—Cercus. K—Yolk. L—Lateral tergal plate. T_{11}—Eleventh tergite.

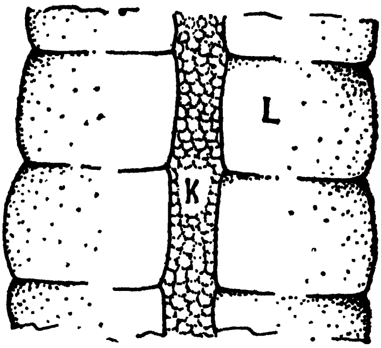

FIG. 57. Dorsal view of a portion of embryonic abdomen, showing the *tergal plates* closing in. ×50.

K—Yolk. L—Lateral tergal plates.

Below are described the structural modifications of the distal abdominal segments, leading to the formation of the genitalia, with their respective homologies in each sex.

Female Embryo

(Figs. 55, 58, 59, 60, 61)

8th Sternum.—The protopodites develop a small lobe on each, which represents the *endopodite* (E). The protopodites bearing the endopodites show a tendency to shift their position in a postero-mesal direction. Towards the end of the embryonic stage, the protopodites fuse completely with the sides of the 8th sternite, while their endopodites take up their final position along the posterior margin of the same sternite, as two oval-shaped sclerites. These sclerites, representing the embryonic

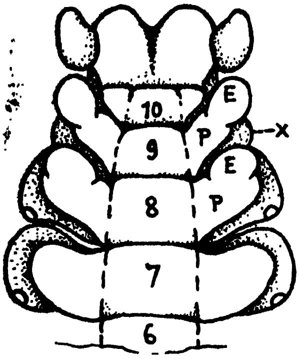

FIG. 58. *Female* embryo : ge 1. ×65.

6—10 Abdominal segmental sternites. E—Endopodite. P—Protopodite. X—Exopodite.

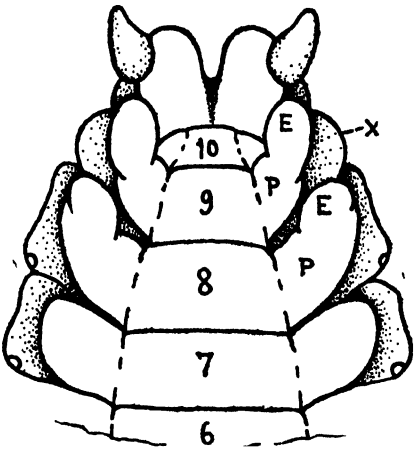

FIG. 59. *Female* embryo : Stage 2. ×65.

(Tenth sternal region gradually passing under the ninth). Lettering as in Fig. 58.

endopodites of the 8th pair of abdominal appendages, give rise to the so-called *ventral valves* of the adult stage. The 8th exopodites (X) bearing the 8th pair of abdominal spiracles form the subtergites of the 8th tergum.

9th Sternum.—The protopodites develop a small lobe on each, which represents the *endopodite* (E). The protopodites bearing the endopodites show a tendency to shift their position in a postero-mesal direction. Towards the end of the embryonic stage, the protopodites fuse completely with the sides of the sternite, while their endopodites take up their final position on the posterior margin of the same sternite, in the form of a pair of conical, slightly curved sclerites. These latter, representing the embryonic endopodites of the 9th pair of abdominal appendages, give rise to the so-called *dorsal valves* of the adult stage. The 9th exopodites do not carry any spiracles. They are relatively smaller than the preceding exopodites. As usual, they contribute to the formation of the 9th subtergal region.

10th Sternum.—The sternite and its protopodites show a tendency to reduction in size, followed by their cephalad migration under the basal region of the 9th pair of appendages. Towards the end of the embryonic stage, the greatly attenuated 10th sternite and its reduced protopodites take up their final position at the base of and between the 9th endopodites. The 10th *endopodites* are at no stage clearly distinguishable, but it is presumed that the two tiny elevations on the 10th sternal region (Fig. 66) which invariably give rise to the *inner valves* of the adult stage, represent the 10th endopodites. The 10th exopodites do not carry any spiracles. They are much smaller than even the 9th pair, and as usual form the subtergal region of the 10th tergite.

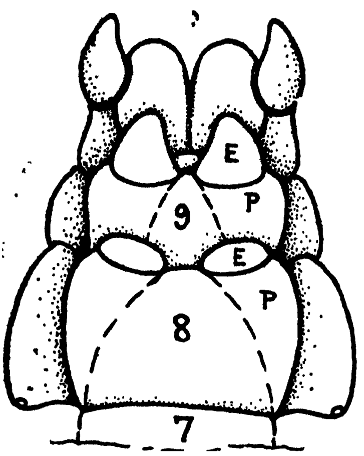

FIG. 60. *Female* embryo : Stage 3. ×50.
(Only a trace of tenth sternite seen from outside).

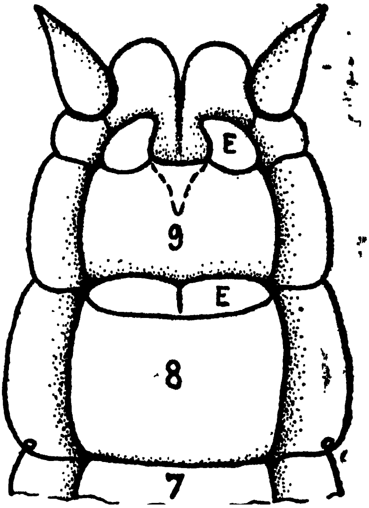

FIG. 61. *Female* embryo : Stage 4. ×45.
(Tenth sternal region hidden completely under the ninth). 8E—Eighth endopodite (ventral valve). 9E—Ninth endopodite (dorsal valve).

11th Sternum.—The sternite, like the preceding one, shows a tendency to reduction in size, followed by its disappearance. Its only vestige in the adult stage is seen in the form of a small Y-shaped sclerite developed in the intersegmental membrane. The *protopodites* (Fig. 55.PP) are extensively developed, are joined to each other at their bases, and represent the so-called *paraprocts* of the adult stage. The *exopodites* of this terminal segment, instead of being fused with the segmental tergite, remain separate in the form of the so-called *cerci* (CR). The endopodites of the terminal abdominal segment are either obscure or not developed at all.

Male Embryo

(Figs. 55, 62, 63, 64, 65)

8th Sternum.—The protopodites flatten out laterally and fuse with the sides of the sternite. The exopodites bear the 8th pair of spiracles and form the subtergites of the 8th tergum. The endopodites are not differentiated at all.

9th Sternum.—The protopodites develop a small lobe on each, which represents the 9th *endopodite* (E). The protopodites bearing the endopodite-lobes show a tendency to grow in a postero-mesal direction. Towards the end of the embryonic stage, the two protopodites fuse completely with the sides of the 9th sternite, while their endopodites take up their final position on the posterior margin of the same sternite, in the form of a pair of slightly curved conical sclerites. It is these endopoditic cones which give rise, in due course, to the so-called *subgenital plate* or the *syncoxite* (Crampton 1925) of the adult stage. The exopodites do not possess any spiracles. Like the preceding ones they form the subtergites of the 9th tergum.

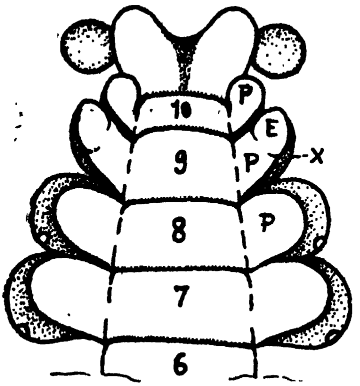

Fig. 62. *Male* embryo: Stage 1. ×65.

6—10 Abdominal segmental sternites.
P—Protopodite. X—Exo-podite.
E—Endopodite.

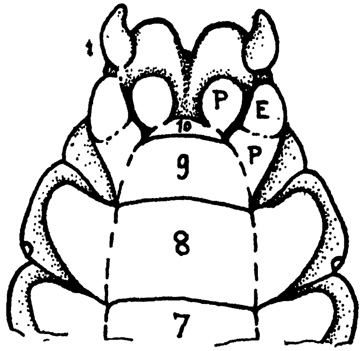

Fig. 63. *Male* embryo: Stage 2. ×65.

(Tenth sternal region gradually passing under the ninth). Lettering as in Fig. 62.

10th Sternum.—The sternite shows a tendency to reduction in size, followed by its cephalad migration under the posterior margin of the 9th sternite. The lobe-like, paired *protopodites* (P) follow the migrating sternite very closely. Towards the end of the embryonic stage, the sternite has almost disappeared from view, and the protopodites have definitely passed under the basal region of the 9th endopodites. These cephalad migrating 10th protopodites, concealed under the 9th endopodites, give rise, in due course, to the so-called *ventral valves* of the adult stage. The 10th endopodites are rather obscure. The 10th exopodites though very much reduced in size, form as usual the subtergal region of the 10th tergum.

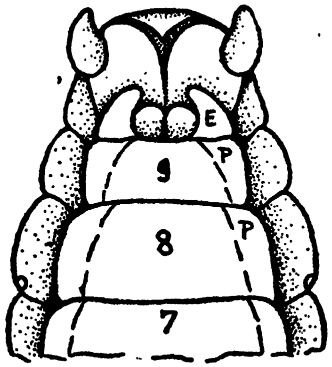

Fig. 64. *Male* embryo: Stage 3. ×50.

(Only the tenth protopodites visible from outside).

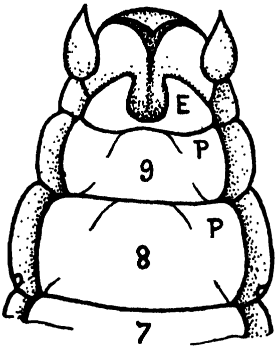

Fig. 65. *Male* embryo: Stage 4. ×45.

(Tenth sternal region completely hidden under the ninth).
9E—Ninth endopodite leading to the formation of syncoxite.

11th Sternum.—The developmental fate of the sternite and its appendages is identical with that of the corresponding female sternite and its appendages described above.

DISCUSSION

Wheeler (1893) has pointed out that the three pairs of valves in the female are serially homologous with the 8th, 9th and 10th pairs of abdominal appendages. He further states that the 10th sternite and its appendages migrate very early in a cephalad direction between the bases of the 9th appendages, a fact which, for want of accurate observations, has undoubtedly misled many a later author (Walker, Nel), in their interpretation of the homologies of the female and the male genitalia. Wheeler's observations, as briefly stated above, are essentially borne out by those of the writer made in *S. gregaria*, as described in this paper.

According to Walker (1919) and Nel (1929), the ventral valves of the female belong to the 8th sternite, while the dorsal and the inner ones belong to the 9th sternite alone. Walker's observations are obviously based on a study of the adult and the nymphal stages of insects. Nel claims to have gone deeper into the embryonic background. But even this author appears to have failed in observing the mesocephalad migration of the 10th sternite and its appendages underneath the 9th, which occurs very early in both the male and the female embryos. That is why the interpretation of the female inner valves and of the male ventral valves by these authors is far from correct. The study of the embryonic development of *S. gregaria* easily shows that the female inner valves are by no means the product of a subdivision of the 9th pair of abdominal appendages. They are definitely derived from the 10th pair, much in the same way as the ventral and the dorsal valves are derived from the 8th and the 9th pairs of abdominal appendages.

Heymons (1895), Crampton (1929), and several authors quoted by Crampton, consider the cerci as the exopodites of the last abdominal segment. Heymons, believing in the theory of a 12-segmented abdomen, takes them to be the exopodites of the 12th segment. Crampton, believing in the theory of a 10-segmented abdomen, considers them to be of the 10th segment. The study of the embryonic appendages of *S. gregaria* reveals that the cerci are appendicular in origin, and that they represent the exopodites of the 11th pair of abdominal appendages, there being only 11 abdominal segments in this Orthopteroid insect.

Chopard (1920) who holds the view of a 12-segmented abdomen of insects, states that the ventral and the inner surfaces of the paraprocts represent the 10th and the 12th sternites. He however mentions nothing regarding the fate of the 11th sternite. Else (1934) considers the podical plates (paraprocts) to be the 11th sternite split into right and left halves by a median slit. The study of the embryo of *S. gregaria* points out that the number of abdominal segments in this Orthopteroid insect is only eleven, that the 11th sternite gets reduced and obliterated, and that the paraprocts are morphologically of an appendicular nature, being homologous with the protopodites of the 11th pair of abdominal appendages.

GENITALIA OF THE POST-EMBRYONIC AND ADULT STAGES

Female Stages

INSTAR I (FIG. 66)

8th Sternum.—The sternite is well developed (S_8). A small transverse aperture is seen in the mid-ventral line nearer the anterior margin of the sternite. It represents the female *genital opening* (GO). Distally a pair of subpyriform lobes (VV) is clearly marked off from the sternite by sutures. They represent the *ventral valves*, homologous with the 8th endopodites.

9th Sternum.—The sternite is well developed (S_9). Along the posterior margin of the sternite is seen a pair of conical lobes, the *dorsal valves* (DV), which are homologous with the 9th endopodites.

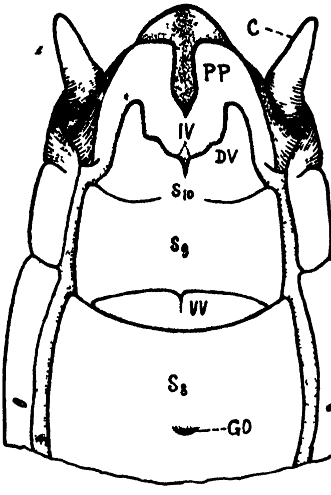

FIG 66. *Female first Instar.* ×35. C—Cercus. DV—Dorsal valve. GO—Genital aperture. IV—Rudiments of inner valves. PP—Paraprocts. S_{8-10}—Segmental sternites. VV—Ventral valve.

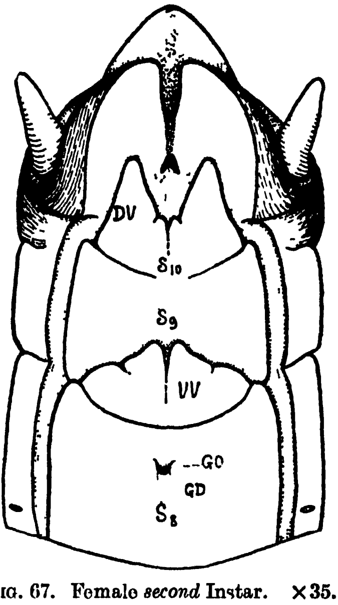

FIG. 67. Female *second* Instar. ×35. GD—Genital duct. Other lettering as in Fig. 66.

10th Sternum.—The sternal region is reduced to a very small area. A pair of minute protuberances is situated on the inner sides of the basal region of the dorsal valves. They represent the rudiments of the *inner valves* (IV), presumably homologous with the 10th endopodites.

INSTAR II (FIG. 67)

8th Sternum.—The female genital aperture (GO) shifts more towards the posterior margin of the sternite. The *oviduct* (GD) leading back from the aperture within the body is well seen in this stage. The ventral valves elongate posteriorly and give rise to a pair of blunt terminal processes which represent the rudiments of the hooks or *styli*. In the suture between the valves is found a small aperture, the *spermathecal opening*.

9th Sternum.—The sternite shows a tendency to shortening. The dorsal valves elongate in the posterior direction.

10th Sternum.—The inner valves are fairly distinct. In the suture between them is seen a minute aperture which represents the opening of the *accessory gland.*

INSTAR III (FIG. 68)

8th Sternum.—The female genital aperture (GO) migrates backward and lies on the posterior margin of the sternite. The posterior margin of the sternite shows a tendency to fold inwards. The ventral valves develop a membranous connecting fold between themselves in which is located the spermathecal opening (SPO).

9th Sternum.—The sternite is much reduced. The dorsal valves elongate still more in the posterior direction. The rudiments of the terminal hooks or *styli* are clearly differentiated.

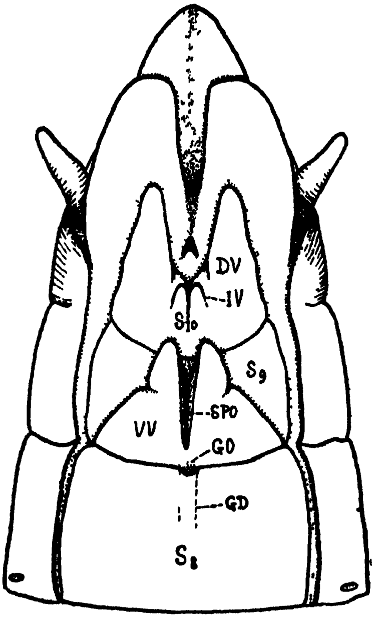

FIG. 68 Female *third* Instar ×25.
SPO—Spermathecal opening.

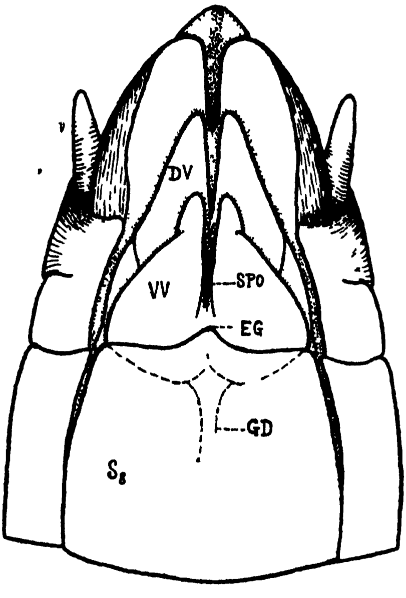

FIG 69 Female *fourth* Instar. ×16.
EG—Egg guide.

10th Sternum.—The inner valves along with their basal sternite shift more and more cephalad between the bases of the dorsal valves. The opening of the accessory gland is clearly seen. A small duct leading inside from the opening is also visible.

INSTAR IV (FIG. 69)

8th Sternum.—The female genital aperture passes underneath the infolded posterior margin of the sternite. The mid-region of the posterior margin of the sternite develops a blunt process known as the *egg-guide*

(GE) or "digitulus" (Boldyrev, 1929). The ventral valves elongate still more posteriorly.

9th Sternum.—The sternite is very much reduced and is hidden under the ventral valves. The dorsal valves elongate still more posteriorly.

10th Sternum.—The inner valves migrate more and more cephalad towards the base of the dorsal valves. They are thus completely hidden beneath the hooks of the ventral valves.

INSTAR V (FIGS. 70, 71)

8th *Sternum.*—The female genital aperture migrates forward underneath the sternite. The portion of the sternite posterior to the genital opening is commonly known as the *sub-genital plate* or lamina (SGP). The egg-guide is fairly elongated and produced behind between the ventral valves. The ventral valves develop secondarily sclerotised areas on their body. The terminal hooks are bent ventrad.

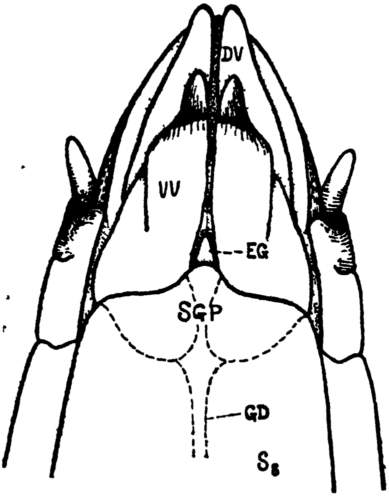

FIG. 70. Female *fifth* Instar. ×10. SGP—Subgenital plate.

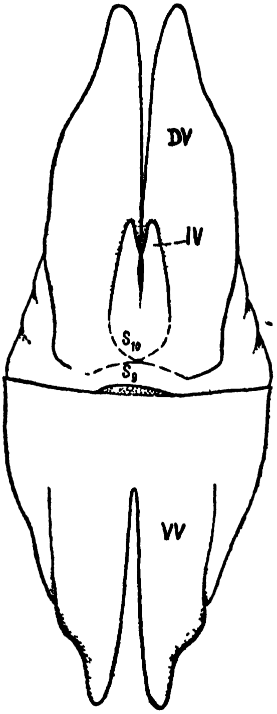

FIG. 71. Female *fifth* Instar: Genital *valves* spread out. ×14.

9th Sternum.—The sternite (Fig. 71. S_9) is reduced to a small, transverse sclerite situated at the base of the dorsal valves. The dorsal valves extend beyond the paraprocts. The hooks are well developed and bent dorsad.

10th Sternum.—(Fig. 71). The inner valves (IV) occupy a definite area between the dorsal valves. The 10th sternite (S10) is limited to a narrow portion situated beyond the 9th sternite, between the dorsal valves.

ADULT STAGE (FIGS. 72, 73, 74, 75, 76, 77, 78)

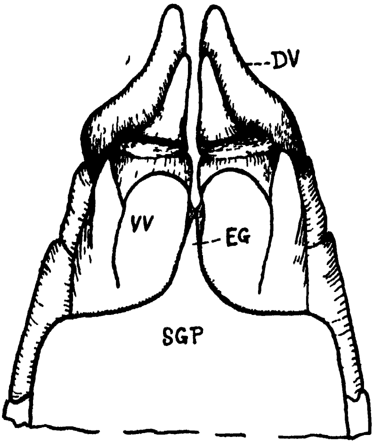

FIG. 72. Female *adult* stage. ×8.
DV—Dorsal valve. EG—Egg-guide
VV—Ventral valve. SGP—Subgenital plate.

8th Sternum.—The female genital aperture known as the *gonopore* or *vulva* (Fig. 73. GO) is situated on the inner surface of the under-folded distal region of the 8th sternite. The subgenital plate (Fig 72. SGP) is quite extensive. The egg-guide (EG) takes the form of a sharply conical process lying against and between the ventral valves. The distal region of the sub-genital plate which is folded under on itself on either side of the egg-guide, forms a pair of chitinous concave plates (Fig. 73. CP) on either side of the gonopore. The concavities of these plates appear like a pair of pocket-like depressions (K). The plates in question develop on their internal surfaces a pair of transverse, ridge-like elevations (Fig. 74. RE) which are strongly chitinised and irregular in outline. These ridges or outgrowths serve probably to prevent

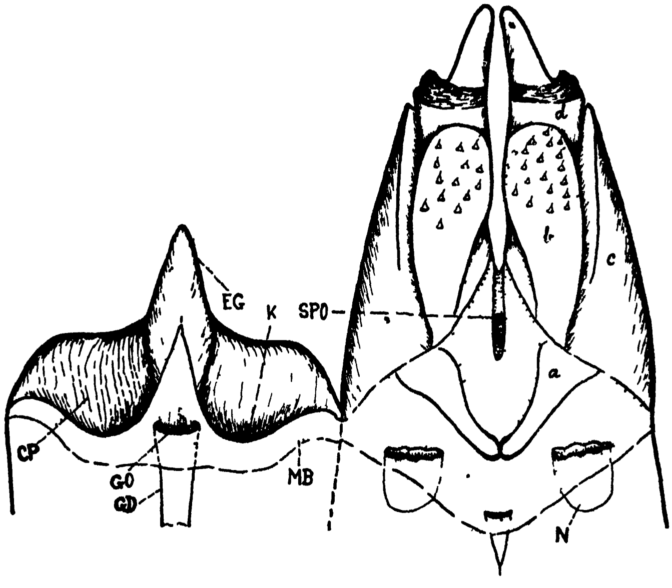

FIG 73. Female adult *sub-genital plate* opened out, exposing genital opening and other structures hidden under it ×10.

a—"Arcus." b—Ventral sclerite. c—"Pileolus." d—Dorsal sclerite. CP—Concave underfolded plate. EG—Egg-guide. GD—Genital duct GO—Genital opening. K—Depression in CP MB—Intermediate membrane. N—Pouch. SPO—Spermathecal opening.

he underfolded plates from resting too closely against the inner sides of the subgenital plate. There extends an ample intermediate membrane (MB) between the distal margin of the underfolded plates and the base of the ventral valves. In this membrane is found a pair of pouch-like pockets (Fig. 73. N) situated laterally. They are provided with muscle-bands, attached at one end to their bottom and at the other to the antero-lateral apophyses of the 8th sternite. Vardé (1929) finds similar pouches in *Anacridium aegypticum* which he names as "vesicules oviductaires." The exact function of these pouches needs however to be investigated.

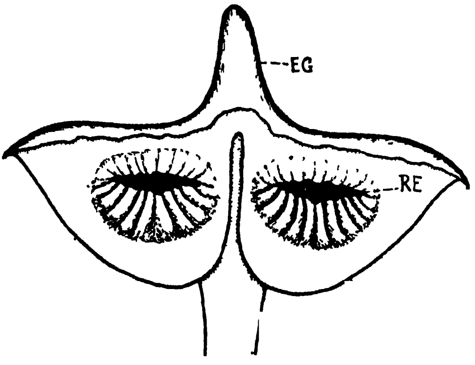

FIG. 74. Female *subgenital plate* cut open, showing ridge-like outgrowths on the inner side of underfolded plates. ×16.

CP—Underfolded plates. EG—Egg-guide. GD—Genital duct. Re—Ridgelike outgrowth.

The *ventral valves* (VV) are apparently situated in the intersegmental membrane between the 8th and the 9th sternal regions. Morphologically, they are homologous with the endopodites of the 8th pair of abdominal appendages. Each valve is an elognated, deeply chitinised structure formed of four sclerotised pieces. Two of these lie on the ventral side, one on the dorsal side, and the fourth is situated laterally. Of the two ventral pieces, the basal one (*a*) is somewhat club-shaped and known as *arcus* (Boldyrev, 1929). Walker interprets it as a portion of the "basivulva"(?). The arcus from one valve meets its mate from the other, and thus they together form a median V-shaped structure, connecting the two valves in the intravalvular membrane. The other ventral sclerite of the valve (*b*) is a large oval piece situated on its meso-ventral side. It carries a number of minute tubercles on its slightly convex surface. The third sclerite (*d*) situated dorsally is greatly elongated, and terminates distally into a strongly chitinised hook called the *stylus* which is curved ventralwards. Proximally it has a broad base which is connected with the *valvifer* (Fig. 75.VL) by means of a small intermediate piece (*e*). The fourth sclerite situated laterally (*c*), and known as the *pileolus* (Chopard, 1920), is the largest portion of the ventral valve. Its dorso-lateral margin grows into a wing-like expansion which, in situ, overlaps the flank of the dorsal valve of each side (Fig. 78). The two valves are joined to each other by an ample intravalvular membrane in the centre of which lies the spermathecal aperture (SPO) located in a cup-like chitinised area.

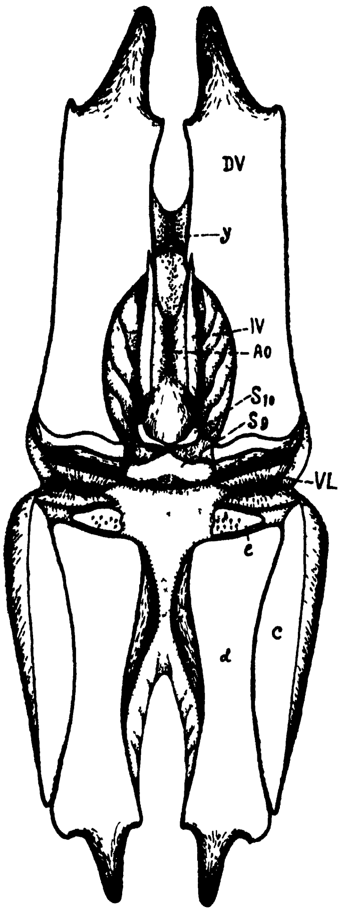

Fig. 75. Female genital *valves* spread out. ×10.
c, d, e,—Sclerites of ventral valve. AO—Accessory gland aperture. DV—Dorsal valve. IV—Inner valve. S_9—Ninth sternite. S_{10} Tenth sternite. VL—Valvifer. Y—Y-shaped sclerite.

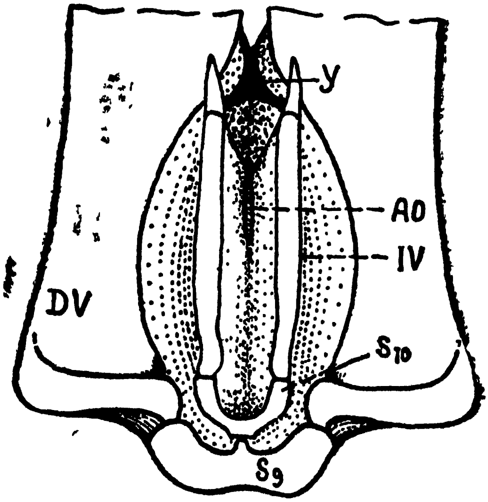

Fig. 76. *Basal region* of dorsal and inner *valves* enlarged. ×20.
Lettering as in Fig. 75.

9th Sternum.—The 9th *sternite* (Figs. 75, 76. S_9) is reduced to a very small, narrow, median sclerite situated at the base of and between the *dorsal valves* (DV). The latter are morphologically homologous with the endopodites of the 9th pair of abdominal appendages. Each valve is formed of a single, hollow, chithinous piece, ending distally into a strongly developed hook (stylus) which is bent dorsad. Proximally the valve is connected with the *valvifer* (VL) along its basal margin. The mesal corner of the base of each valve is immovably joined to the side of the 9th sternite. There are no secondarily formed areas on the dorsal valves, like those on the ventral valves. Laterally each dorsal valve sends inwards a pair of *apophyses* (Fig. 77. AP) of which the dorsal one is longer and more strongly developed. Between the two valves extends an ample intra-valvular membrane in which are situated the various parts of the 10th abdominal sternum. The *valvifer* (Figs. 75, 78. VL) is a long blade-like apophysis arising from the basal region of the dorsal and the ventral valves on each side, and stretching cephalad, within the body-cavity.

10th Sternum.—The tenth *sternite* (Figs. 75, 76. S_{10}) is represented by a very small, arch-like sclerite situated behind the 9th sternite, in the intravalvular membrane of the dorsal valves. The *inner valves* (IV) extend behind from the lateral ends of the arch-like sternite, and are homologous with the endopodites of the 10th pair of abdominal appendages. Each valve has the form of a chitinous rod ending distally into a fine process representing the *stylus*. The valves, all along the proximal portion of their length, remain attached to the intravalvular membrane between the dorsal valves. The space between the inner valves is occupied by another intravalvular membrane in the centre of which is situated the opening of the *accessory gland* (AO). The latter is rather vestigial in this locust, though functional in Blattidæ (Nel, 1929). The special feature of the tenth sternal region of this Orthopteroid insect consists in the great reduction in size of the sternite and of its appendages, their meso-cephalad migration, and their lodgement in the intravalvular membrane of the 9th pair of appendages.

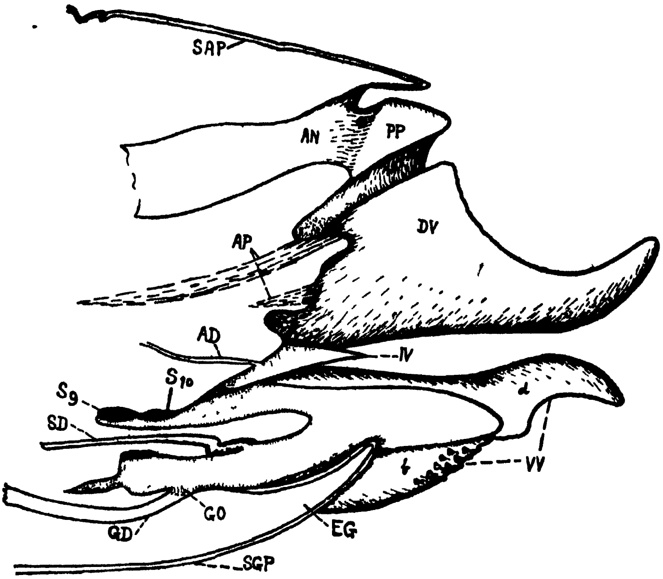

FIG. 77. *Mid-vertical section* through genital and anal regions of *female* adult (semi-diagrammatic). ×14.

AD—Accessory duct. AN—Anus leading into rectum. AP—Apophyses. DV—Dorsal valve. EG—Egg-guide. GD—Genital duct. GO—Genital opening. IV—Inner valve. PP—Paraprocts. $S_{9 \cdot 10}$—Ninth and tenth sternites. SAP—Supra-anal plate. SD—Spermathecal duct. SGP—Subgenital plate.—VV—Ventral valve.

11th Sternum.—Situated in the distal region of the intravalvular membrane of the dorsal valves is seen a small, median, *Y-shaped sclerite* (Figs. 75, 76. Y) which is probably the *vestige* of the 11th sternite. The chitinisation of the local membrane giving rise to the sclerite is observed only from the II Instar. The *paraprocts* (PP) are somewhat triangular in form, all the three surfaces of each being thinly chitinised. They represent the 11th *protopodites.* The *cerci* (C) are blunt conical processes representing the 11th *exopodites.*

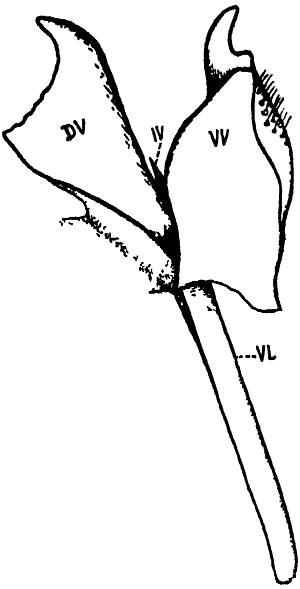

FIG. 78. Lateral view of female valves showing *valvifer* ×7. DV—Dorsal valve. IV—Inner valve. VV—Ventral valve. VL—Valvifer.

Bodenheimer (1929) has shown in his studies on this locust that the hoppers usually undergo their moult just when they have doubled their size and volume compared with the preceding Instar. Data given below in respect of the female valves confirm the view reached by that author.

Table giving the length-measurements of the female valves in the various Instars

Instar	I	II	III	IV	V	Adult
Ventral valves ..	.17 m.m.	.35	.71	1.42	2.70	5.32 m.m
Dorsal valves .	.22 m.m.	.46	.96	1.86	3.42	6.34 m m
Inner valves .	.05 m.m.	.12	29	.62	1.22	2.43 m m.

Male Stages

Unlike the female, the 8th sternum and its appendages of the male take no part in the formation of the male genitalia. Their developmental fate has already been described on page 8. Unlike the female, the 9th sternite together with its laterally fused protopodites of the male persists as a well-developed structure throughout the postembryonic and the adult stages ; while its endopodites give rise to a united, extensive, boat-shaped and terminally bifid structure called the *syncoxite* (Crampton, 1925), also called as the *subgenital plate*, which remains attached to the posterior margin of the sternite. The 10th sternal region shows a tendency to shorten and pass under the syncoxite of the 9th sternite. Towards the end of the embryonic stage, the 10th sternite disappears completely. Of its appendages, only the protopodites persist which develop into the ventral valves of the male genitalia.

INSTAR I (FIG. 79)

The *9th sternite* (S_9) is well-developed. Its *endopodites* are indistinguishably fused with each other, and thus form the *syncoxite* (SN). Only their tips remain separate giving rise to a bifid structure. The suture joining the syncoxite with the sternite is incomplete medially. There is no trace of the 10th sternite. Its protopodites, hidden under the 9th syncoxite, unite with each other along a median suture, and thus jointly represent the *ventral valves* (VV) of the male genitalia.

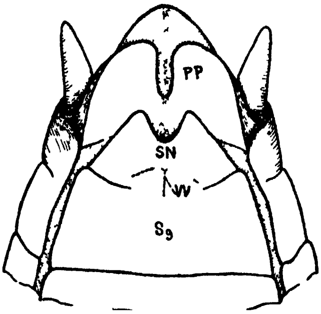

FIG. 79. Male *first* Instar. ×32
PP—Paraprocts. S_9—Ninth sternite. SN—Syncoxite. VV—United ventral valves (hidden under SN).

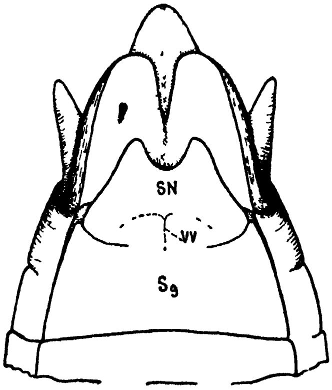

FIG. 80. Male *second* Instar. ×30.
Lettering as in Fig. 79.

INSTAR II (FIG. 80)

The syncoxite elongates in a posterior direction. The united ventral valves (VV) begin to get chitinised. The intermediate membrane between the ventral valves and the paraprocts shows a small median aperture which represents the *male genital opening*.

INSTAR III (FIG. 81)

The syncoxite elongates more and more posteriorly. The ventral valves become still more chitinised. The intermediate membrane shows

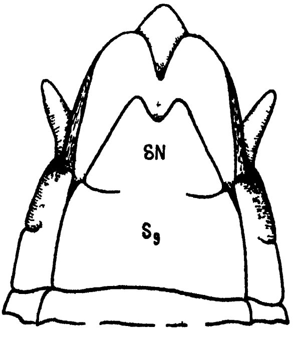

FIG. 81. Male *third* Instar. ×20·

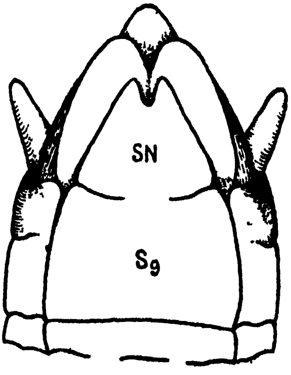

FIG. 82. Male *fourth* Instar. ×1.

a secondary chitinisation round the male genital aperture, particularly on the dorsal side. The chitinised area represents the rudiments of the *dorsal valve*. Postero-dorsal to the rudimentary dorsal valve, the intermediate membrane shows a depression on the floor of which develops a slightly chitinised area, the rudiments of the *epiphallus*.

INSTAR IV (FIG. 82)

The intersegmental membrane between the distal end of the syncoxite and the base of the united ventral valves grows extensively and is known as the *pallium*. The rudiments of the dorsal valve and the epiphallus increase in area and become more chitinised.

INSTAR V (FIG. 83)

The syncoxite extends posteriorly as far as the tips of the paraprocts. The ventral valves assume a definite hood-like or wig-like form. The dorsal valve also becomes more chitinised, and sends from its basal corners a pair of chitinous apophyses within the body-cavity for muscle-attachment. The genital tube takes a definite position between the dorsal and the ventral valves. The membranous rim of the genital opening becomes slightly chitinised. No other structures of the penial apparatus are developed as yet.

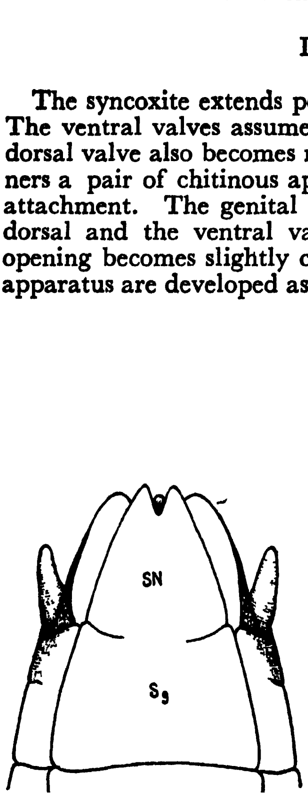

FIG. 83. Male *fifth* Instar. ×10.

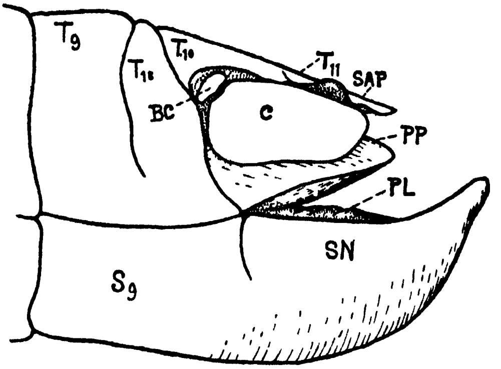

FIG. 84. Male *adult* stage, lateral view. ×10. BC—Basicercus. C—Cercus. PL—Pallium. PP—Paraprocts. S_9—Ninth sternite. SAP—Supra-anal plate (T_{11}). SN—Syncoxite. T_{9-11}—Segmental tergites.

ADULT STAGE (FIGS. 84, 85, 86, 87, 88, 89, 90)

The *syncoxite* of the adult stage (Fig. 84. SN) extends much beyond the paraprocts. It is a very prominent structure, boat-shaped in form bifid at the apex, and convex externally. Morphologically, it is formed by the fusion of the *9th endopodites*. Walker (1922) names it as the "coxosternum;" while Crampton (1925) designates it as the "syncoxite." But both these terms appear to be rather misleading, in view of the different homology of the structure concerned. The term "subgenital plate," though a little lengthy, is however more significant, particularly from the descriptive point of view. On account of the excessive development of the syncoxite in the adult stage, the genital area is gradually shifted from the ventral to the antero dorsal position. Consequently all the principal structures of the male genitalia lie within the cavity of the syncoxite which, therefore, automatically, becomes the *subgenital plate* (Figs. 84, 85). The pallial and the intermediate membranes are extensively developed, which by means of their hood-like folds close over the genitalia and thus conceal them from view.

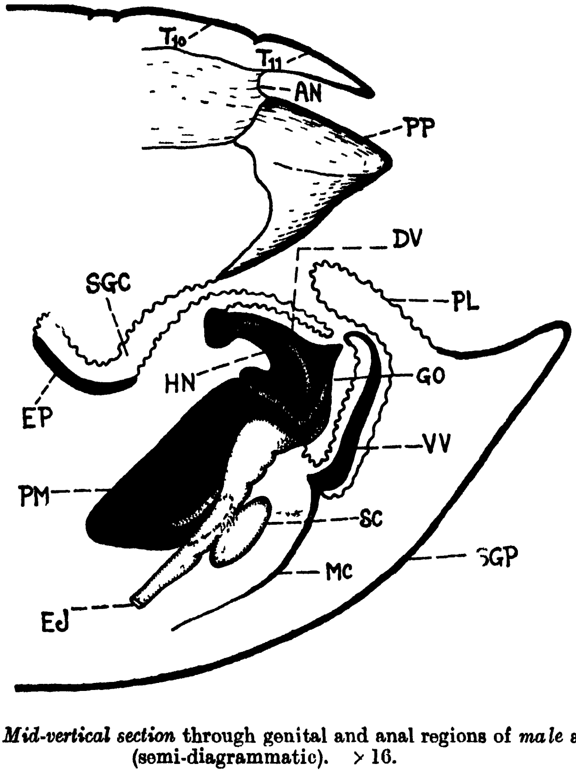

FIG. 85. *Mid-vertical section* through genital and anal regions of *male* adult (semi-diagrammatic). × 16.

AN—Anus. DV—Dorsal valvular sclerite. EJ—Ejaculatory duct. EP—Epiphallus. GO—Genital opening. HN—Horn-shaped octoparamere. MC—Membranous apodeme. PL—Pallial membrane. PM—Endoparamere. PP—Paraprocts. SC—Spermatophore sac SGC—Supra-genital cavity. SGP—Subgenital plate. T_{10}, T_{11} —Segmental tergites. VV—United ventral valves.

The *male genitalia* consist of (1) the united ventral valves, (2) the dorsal valve, (3) the penial apparatus and (4) the epiphallus.

1) *United Ventral valves* (Figs. 85, 86, 87. VV) :

Morphologically, the *valves* (VV) are formed by the 10th pair of *protopodites* united with each other along their mesal margins to develop into a single, convex, wig-like, valvular structure with a broad crescentic base The line of union is marked by the presence of a median suture (SU) with a strong corresponding internal ridge. The basal corners of the united ventral valves are movably attached to the shoulders of the dorsal valve (Fig. 86). From the cresentic base of the ventral valves arises a membranous *apodeme* (Fig. 85. MC) which hangs freely within the cavity of the boat-shaped syncoxite and serves for muscle-attachment. The muscles attached to this apodeme regulate the movement of the united ventral valves which are pulled backwards so as to make the partially shielded penial apparatus project out during copulation. The inner side of the valve is lined by a thin ample membrane which spreads between them and the distal region of the penial apparatus.

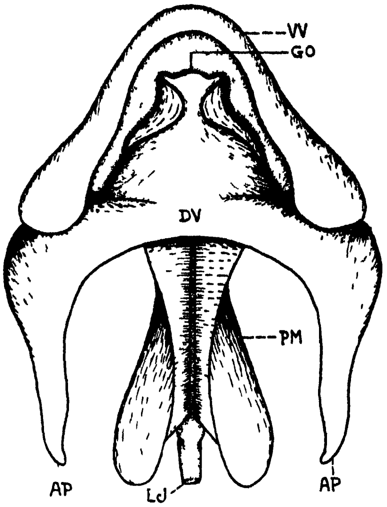

FIG. 86. *Male genitalia,* dorsal view. ×25. AP—Apophyses. DV—Dorsal valvular collar-like sclerite. EJ– Ejaculatory duct GO—Genital opening. PM—Endoparameres. VV—United ventral valves.

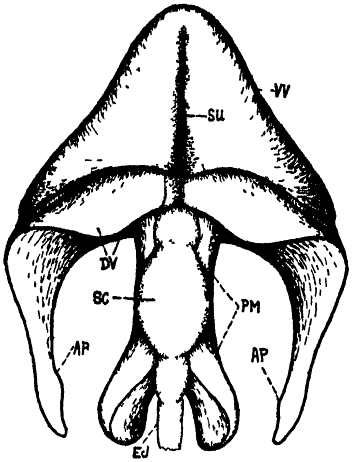

FIG. 87. *Male genitalia,* ventral view. ×22. SC—Spermatophore sac. SU—Suture uniting ventral valves. Other lettering as in Fig. 86.

2) *Dorsal valve* (Figs. 85, 86, 87. DV) :

The *dorsal valve* ('Pont posterieur' of Chopard, 1920) is not, in point of fact, a valvular structure. It is formed of a strongly chitinised, collar-like sclerite, surrounding the distal region of the penial apparatus and firmly cemented to it on all sides. The dorsolateral corners of this sclerite, which are rather broad and shoulder like, serve as fulcri for the movement of the ventral valves, as mentioned above. These corners are produced within the body-cavity in the form of a pair of a strongly chitinised *apophyses* (AP). The muscles attached to these apophyses control the in-and-out movement of the penial apparatus. Morphologically, the dorsal valvular sclerite is the product of a secondary chitinisation of the intermediate membrane situated between the united ventral valves and the paraprocts.

3) *Penial apparatus* (*Aedeagus*) (Figs. 85, 86, 87, 88, 89) :

The penial apparatus consists of four different structures which are all firmly cemented to one another. They are as follows :—

(*a*) A pair of elongated and vertically flattened plates called the *parameres* (Fig. 88. PM). They are fused along their mid-ventral margins to form a trough-like passage for the ejaculatory duct. The distal ends of the parameres are produced to form a pair of narrow, blunt processes (P) which are curved ventrad. Walker (1922) has named the parameres as *endoparameres*.

(*b*) The *ejaculatory duct* (EJ) which is formed of elastic, leathery chitin and which runs through the trough-like passage along the junction of the parameres to which it is firmly cemented. It opens to the outside by an elongated oblique aperture called as the *male genital opening* (Fig. 89. GO). Proximally it carries an oval *spermatophore sac* (SC) on its ventral surface.

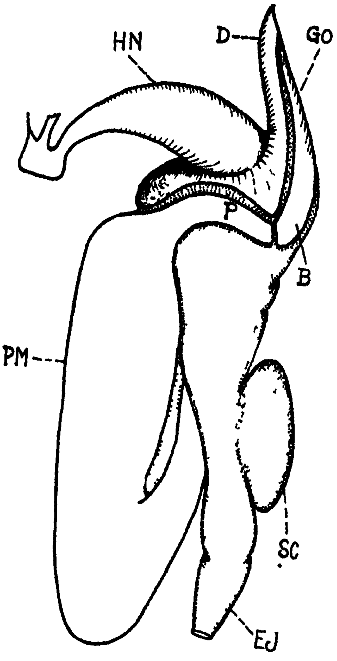

FIG 88 *Penial apparatus*, lateral view ×40

B—Paired ectoparamere bars D—Scooped process of HN (ectoparamere) Other lettering as in Fig 85

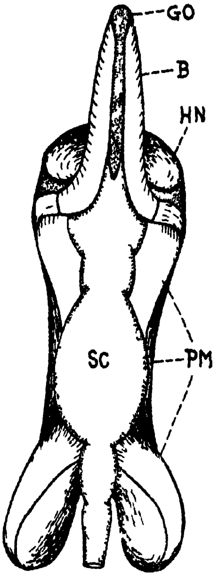

FIG 89 *Penial apparatus*, ventral view ×35

B—Paired ectoparameres bounding genital opening GO—Male genital opening Other lettering as in Fig 88

(*c*) A pair of chitinised bars (Figs 88, 89 B) which support the sides of the genital opening (GO) They are named *ectoparameres* by Walker, and "phallomeres" by Snodgrass (1937).

(*d*) A horn-shaped, strongly chitinised, solid sclerite (HN). Its distal portion (D) is scooped within and forms the roof of the elongated genital opening (GO) The stalk of the horn-shaped sclerite is basally fused with the dorsal valve The sclerite in question is named as *ectoparamere* by Walker, and "phallomere" by Snodgrass (1937)

All these structures (Endoparameres, Ectoparameres and Ejaculatory duct) of the penial apparatus, together with the dorsal valvular sclerite, are immovably fixed to one another, so that they all work as a single compound organ against the united ventral valves.

Regarding the homology of the penial structures, it may be stated that they all arise as the product of a secondary chitinisation of the intermediate membrane between the united ventral valves (10th protopodites) and the paraprocts (11th protopodites), in order to protect and strengthen the region of the male genital opening. Else (1934) regards these structures including the epiphallus as out-growths of the 10th abdominal sternum, a view which appears to be highly improbable, and which is not borne out by observations made in *S. gregaria*.

4) *Epiphallus* (Figs. 85, 90. EP) :

It consists of three chitinised plates and a pair of strong hooks, all situated on the floor of the supra-genital cavity (Fig. 85. SGC) which in itself is formed as the result of the folding of the ample intersegmental membrane above the genital region. Of the three plates, the medium sclerite (M) which is the largest, is placed transversely on the floor and has its anterior corners drawn out in the form of rounded lobes (D). The remaining two sclerites (L) are smaller in size, somewhat triangular in form, and occupy the flanks on either side of the median plate. From the posterior corners of the median sclerite arises a pair of conical, hooklike processes (VP) which stand out at an angle to the median plate. They are known as the "hook-like depressors" of the epiphallus (Boldyrev, 1929).

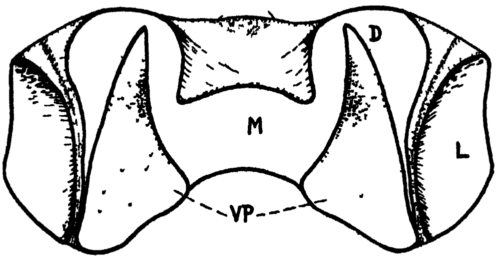

FIG. 90. *Epiphallus.* ×26.
D—Dorsal lobe. L—Lateral sclerite. M—Median sclerite.
VP—Ventral hook-like process.

According to Boldyrev, the epiphallus plays its part in the process of copulation. It "serves firstly to raise the subgenital lamina (plate) of the female into a vertical position, and secondly to compress the anal region of the male."

Walker (1919) names the epiphallus as the "pseudosternite," without however stating its exact homology. Morphologically, it is found to be the product of a secondary chitinisation of the intermediate membrane between the paraprocts and the penial apparatus. From this, one may therefore venture to say that it almost represents the 11th abdominal sternite of the male.

PERIANAL REGION

The study of the development of the terminal abdominal tergites is productive of certain interesting facts. It has already been pointed out that the number of abdominal segments of the embryo of *S. gregaria* is eleven, and correspondingly there are only 11 tergal sclerites. But in the postembryonic and adult stages of the locust, one however finds twelve tergal plates instead of the original eleven. This has often led to a good deal of confusion regarding the actual number of abdominal segments in insects. It is therefore necessary to investigate this question as to *when* and *how* this modification from eleven to twelve tergites takes place in the ontogenetic history of the insect under study.

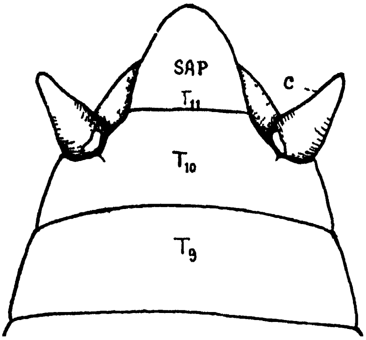

FIG. 91. *First* Instar hopper, just after intermediate moult. ×34. C—Cercus. SAP—Supra-anal plate. T_{9-11}—Segmental tergites.

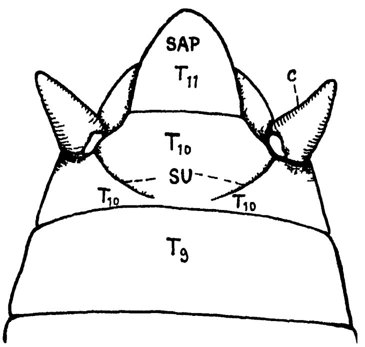

FIG. 92. *First* Instar, about 2 hours after intermediate moult ×34. SU—Secondary sutures dividing tenth tergite (T_{10}).

If a freshly hatched hopper of the I Instar be examined under the binocular microscope, one finds only eleven tergal sclerites, the eleventh

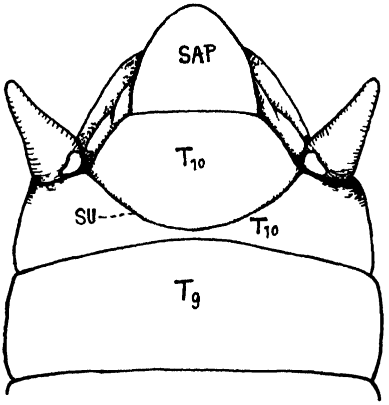

FIG 93. Male *first* Instar, about 4 hours after intermodiate moult. ×26.

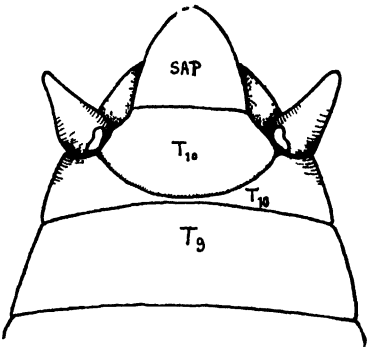

FIG 94 Male *second* Instar. ×26.

being the supra-anal plate (Fig. 91. SAP, T_{11}). But an examination of the same hopper, only a few hours later, reveals the presence of a pair of secondary folds or sutures (Fig. 92. SU) on the surface of the 10th tergite (T_{10}). The folds in question arise in the angle of the cercus pit, and run diagonally in a meso-cephalad direction. In a later stage of the same Instar, the folds on either side meet one another, forming an arch and thus falsely dividing the 10th tergite into two distinct sclerites

(Fig. 93). Failure to trace correctly the origin of these folds dividing the primary 10th tergite into two secondary sclerites, has obviously led many a morphologist to miscount the number of abdominal tergites of Orthopteroid insects. It appears to be particularly so in the case of those who have been advocating the theory of a 12-segmented abdomen of insects.

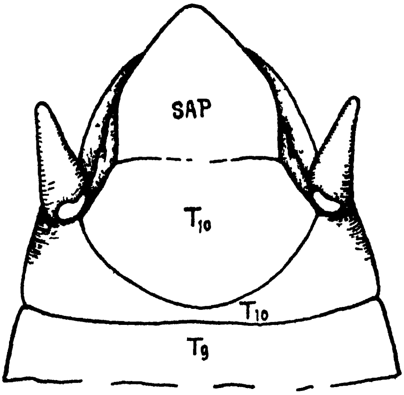

FIG. 95. Male *third* Instar. ×26.

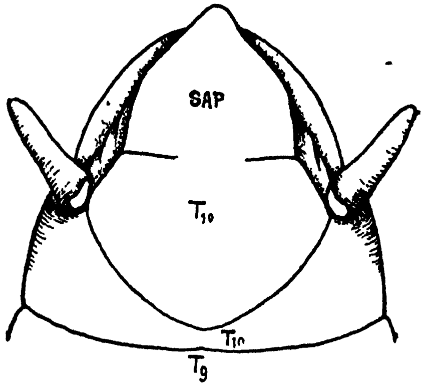

FIG. 96. Male *fourth* Instar. ×20.

Of the two secondarily formed sclerites of the 10th tergum, the proximal one is narrow in the mid-dorsal region and broad laterally. It is immovably connected with the 9th tergite by means of the intersegmental suture which is incomplete laterally in the adult stage (Fig. 84). The distal sclerite of the 10th tergite is somewhat pentagonal in form. The intersegmental suture between it and the 11th tergite is persistent in all the stages of the *female* locust (Figs. 99-104). In the case of the *male*, however, the suture in question shows a tendency to gradual disappearance through the post-embryonic Instars (Figs. 91-97), and in the adult stage it is almost obscure except for the vestigial lateral clefts present in that region (Fig. 98).

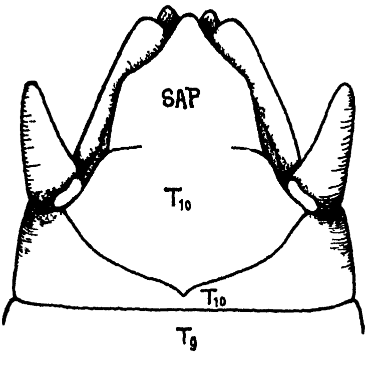

FIG 97 Male *fifth* Instar. ×14.

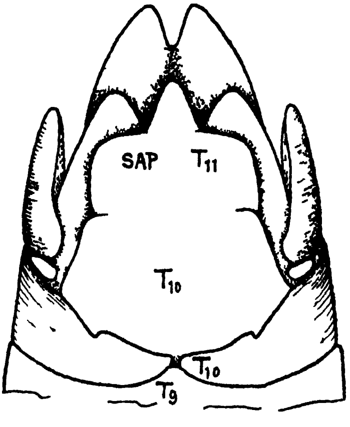

FIG 98 Male *adult* stage ×10.

The 11th tergite known commonly as the *supra-anal plate* (SAP, T_{11}) shows certain variations in its shape in the two sexes. In the *male* the tergite in question is somewhat dome-shaped in the I and II Instars (Figs. 93, 94). In the III, IV and V Instars it becomes gradually subcordate and develops a bluntly conical tip (Figs. 95, 96, 97). In the adult stage (Fig. 98) the posterior corners of the plate widen out, and between them projects behind a median sharply conical process. In the *female*, the general shape of the supra-anal plate is conical, which it maintains in all the stages of the locust (Figs. 99-104).

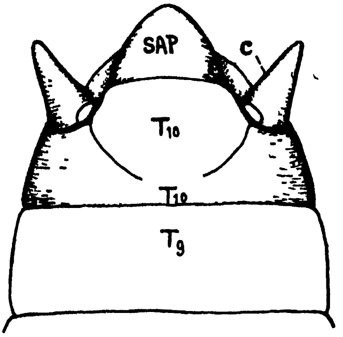

Fig. 99. Female *first* Instar, a few hours after intermediate moult. × 34.

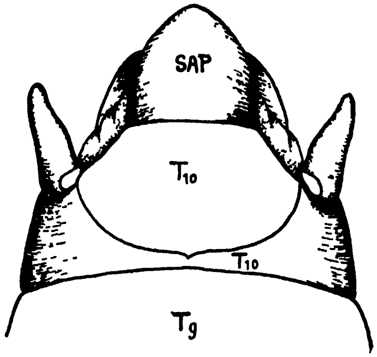

Fig. 100. Female *second* Instar. × 34.

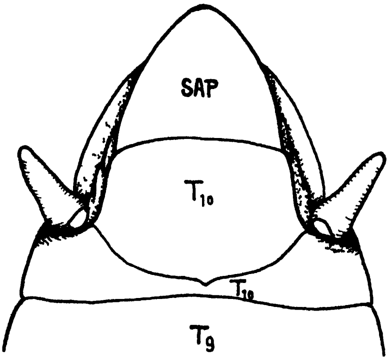

Fig. 101. Female *third* Instar. × 26.

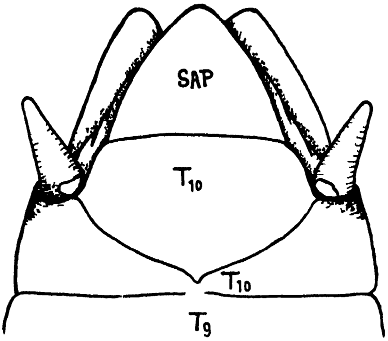

Fig. 103. Female *fifth* Instar. × 16.

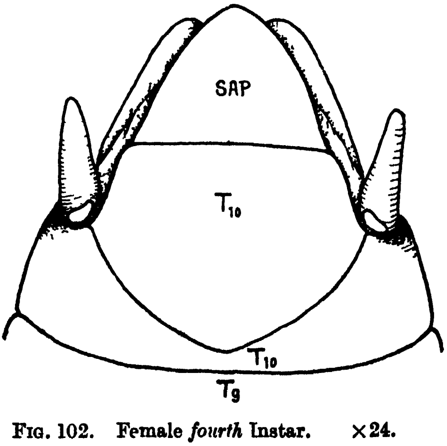

Fig. 102. Female *fourth* Instar. × 24.

Another interesting feature of the perianal region relates to the development of the *cerci*. These structures are, as already mentioned, homologous with the exopodites of the 11th pair of abdominal appendages. In the first Instar each cercus is somewhat pyramid-like in form with an oval base which gradually tapers to a conical tip (Figs. 93, 99. C). In the case of the *female* the cercus retains this form in all its stages without any change except in size. In the case of the *male*, however, the cercus becomes gradually flattened laterally and increases in size and length much more than in the female. The average length of the male cercus is 2.1 m.m., while that of the female one is 1.2 m.m. The cerci are all covered with long flexible hairs and are presumed to be organs of sense. In the dorsal corner of the base of each cercus is situated a small sclerite known as the *basicercus* (BC). Morphologically it is the product of a secondary chitinisation of the basal membrane. It is also covered with very minute scaly structures.

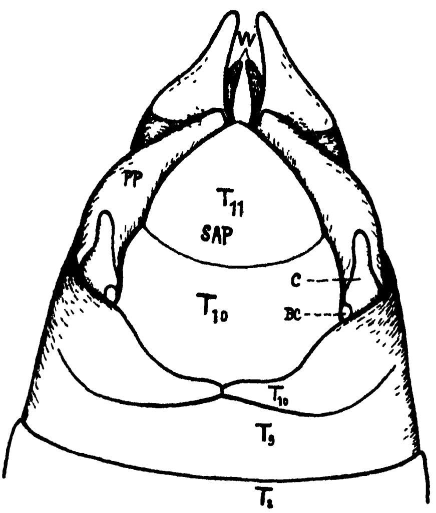

FIG. 104. Female *adult* stage. ×10.

SUMMARY

The ontogenetic studies of the abdominal structures of *S. gregaria* with special reference to the genitalia, clarify the following points :—

1) The presence of eleven abdominal segments in the embryo of the locust.

2) The presence of eleven pairs of the Crustacean type of segmentally arranged abdominal appendages in the embryo of the locust.

3) The fusion of the proximal appendages with the sides of the sternal and tergal plates in the embryo.

4) The modification of the distal sternites and appendages leading to the formation of the genitalia.

5) Great reduction in size of the 10th sternite and its appendages followed by their meso-cephalad migration between the 9th appendages.

6) The three pairs of valves of the female ovipositor are serially homologous with the paired appendages of the 8th, 9th and 10th segments.

7) The male genitalia are mostly the product of a secondary chitinisation of the intermediate membrane situated between the 10th and 11th appendages, only the united ventral valves being homologous with the 10th protopodites.

8) The paraprocts and the cerci are respectively homologous with the embryonic protopodites and the exopodites of the 11th pair of abdominal appendages.

9) The 10th tergum is secondarily divided into two tergites in the early postembryonic stage of the locust, giving an undue cause for an incorrect count of the abdominal tergites.

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A STUDY OF COLCHICINE INDUCED POLYPLOIDY IN PHASEOLUS RADIATUS L.

By

L. S. S. KUMAR AND A. ABRAHAM

College of Agriculture, Poona

ABOUT half the species of investigated angiosperms are polyploids, as inferred from the presence of chromosome numbers in multiples of that found in some related species. While this is the case in nature, the attempt to artificially induce polyploidy has met with any marked success only recently (Blakeslee and Avery, 1937). Of the many methods tried to uniformly double the chromosome number and thus obtain seeds with the doubled number, the application of the alkaloid Colchicine has proved to be the most efficient and the one so far found to be of the greatest general application. Intensive work in this new field is in progress in America (Blakeslee, 1941), where in a number of garden plants and in some crop plants artificial polyploids have been produced. But so far we have come across only five reports on successful application of Colchicine on Indian crop Plants (*Cf.* Pal and Ramanujam, 1939; Amin, 1940; Richharia and Persai, 1940; Pal, Ramanujam and Joshi, 1941; and Ramanujam and Joshi 1942).

The present paper deals with the technique adopted in inducing polyploidy in *Phaseolus radiatus* L. (*Mug*) and a comparison of the diploid and tetraploid as regards certain cytological and anatomical details. Similar experiments on a number of other crop plants are in progress.

MATERIAL AND TECHNIQUE

The seeds of *mug* used for this experiment were from a sample received from the Superintendent, Pusa Research Station (No. 1-P. 18). In the application of Colchicine, various methods are used (*Cf.* Derman, 1940). The optimum dosage and the best method of application of Colchicine varies from species to species. Kostoff and Chevalier (1939) have stated that cereals respond most readily to treatment, Composites are intermediate while Legumes are least sensitive. We tried three methods of applying Colchicine, with varying degrees of success.

(1) *Seed treatment* :—

Seeds were soaked in eight different concentrations of Colchicine solutions between 0.05% and 1% and the treatment was applied for from 24 hrs. to 48 hrs. after which they were transplanted to small earthen pots. An equal number with controls was transplanted in the field also. In all treated seeds the hypocotyl and cotyledons were swollen, the degree of swelling and parallel stunting of growth increasing with the dosage. Some of the seedlings were grown in nutrient solutions for comparison. All concentrations above 0.05% proved lethal, though the seedlings survived for as long as a fortnight in some cases, without putting forth any fresh leaves or showing any marked signs of growth.

Of the seeds treated in 0.05% only three plants survived (Fig. 2). This showed considerable stunting of growth as compared with the normal (Fig. 1). Pollen examination revealed that only one branch of one of the plants was really tetraploid, while others remained diploid. The seedlings grown in culture solution showed that the root development was equally retarded and no secondary roots were formed. Thus the chief cause of failure of this method appears to be the drastic effect on roots. In this connection it may be noted that roots react readily to treatment with various chemicals and produce polyploid cells (Blakeslee, 1941).

(2) *Bud treatment with Colchicine solution* :—

This method consisted in external application of Colchicine solution to the apical bud of the young seedling. Seeds were germinated in pots of convenient size and after the first pair of leaves had expanded properly, a wad of cotton wool was placed on the apical bud and drops of Colchicine solution of 0.2 and 0.4% applied. The seedlings were covered with a bell jar for about 6 hrs. and occasionally additional drops of Colchicine added on the cotton wad. This treatment, like the one described below, allows normal root development while only the shoot portion is affected. One tetraploid plant was obtained from ten seedlings treated in this manner.

(3) *Agar-Colchicine treatment of bud* :—

The method we found most successful with *mug* was applying 0.4% Colchicine in Agar to the apical bud. Small strips of Agar (enough to make 2 to 3%) were boiled in 0.4% Colchicine solution in distilled water. When the Agar-Colchicine mixture had cooled to about 35°C, it was applied to the apical bud and to the axils of the first pair of leaves of seedlings raised in pots as in the previous treatment. The Agar solidifies on cooling and it is best applied while warm. Drops of 0.4% Colchicine are applied to the Agar coating on the bud, every hour, for 4 to 6 hours. The Agar later dries up into a film and peels off as the bud develops. This treatment stunts the growth of the bud considerably and its development is delayed very much. By treating in the above manner we got four plants out of twenty definitely tetraploid, while from some others not examined critically, a mixture of diploid and tetraploid seeds may be expected. Examination of epidermis of strictly comparable leaves (the first fully opened leaf below the apical bud in comparable branches) showed that in at least one plant octoploidy had resulted. The pollen of this plant was not examined and so whether it was only an octoploid chimera (periclinal) could not be ascertained.

CYTOLOGICAL EXAMINATION

Chromosome counts were made from root tips obtained from seeds of the artificial tetraploid (as determined earlier from pollen examination) and the diploid controls. Root-tips were fixed in "Craf" and sections stained in Hæmatoxylin according to a modification of Earle's* (1939 method—this staining gives a light bluish black stain to the cell walls) and to nuclei. After washing for about ten minutes the slides are again stained in gentian violet according to the usual schedule. This superimposing of gentian violet stain on a light background of Hæmatoxylin gives a very contrasting preparation good for photomicrography as well as visual examination. In the cells of the diploid there are twenty-two chromosomes while in the tetraploid there are forty-four chromosomes. Figs. 15 and 16 are photomicrographs showing metaphase plates from cells of the diploid and tetraploid respectively, while Figs. 15-a and 16-a are Indian Ink drawings made on similar photographic prints (see Nayler, 1931). In favourable metaphase plates in the diploid root, 2 satellited chromosomes were seen, though due to the smaller size of the chromosomes, the four satellited chromosomes which should be expected in an auto-tetraploid were not distinguished in the cells of the tetraploid. But in prophase nuclei in many cells of the tetraploid it was found that four chromosomes are attached to the nucleolus thus indicating the presence of four nucleolar chromosomes. Also the nucleolus in the tetraploids is larger than in the diploid.

In one portion of a tetraploid root we found many octoploid cells. This was determined both from size of cells as well as chromosome counts (Figs. 18 and 18-a). In root tip sections it was noticed that cell size and nuclear size from comparable layers usually give an indication of the chromosome number. But the size of individual chromosomes decreases with increase in number. Thus, diploid cells show the largest chromosomes and octoploid the smallest, while tetraploid show intermediate size.

Transverse sections of leaflets of comparable age and development show that tetraploids have thicker leaves, larger cells and plastids than the diploids (Figs. 9 and 10). This gives the leaves a distinctly greener appearance and is a fairly accurate guide in distinguishing affected branches from unaffected ones.

Epidermis from strictly comparable leaves shows an increase in size of cells and stomata in the tetraploid while the number of cells is less (Figs. 7 and 8).

* The slides are mordanted in a mixture of 5% Ferric ammonium sulphate and 5% Ferrous amonium sulphate for about 10 minutes and then stained for 1 to 2 minutes in Hæmatoxylin (½ gm. dissolved in 25 cc. methyl-alcohol plus 25 cc. glycerine), and then it is distilled very well in the mordant diluted twice with water.

ACTION OF COLCHICINE

The observations of Nebel (1937), Nebel and Ruttle (1938), Levan (1938), and others have shown that in a dividing nucleus, Colchicine inhibits the formation of the spindle without affecting chromosome division. Due to this failure of spindle formation the daughter chromosomes do not move to opposite poles and no cell division takes place. The original cell has a reconstituted nucleus with double the chromosome number. This process takes place only in dividing nuclei and Colchicine apparently does not affect resting nuclei. The number of times this process of chromosome doubling may be repeated in a cell is not known, but the observation of 500 to 1000 chromosomes in a single cell of Allium (Levan, 1938) shows that this process may take place several times.

Growth in flowering plants is mainly by the division of a group of meristematic cells and as simultaneous division of all nuclei does not take place even in active meristem such as is found in the apical portion of seedlings, some cells are affected differently from others. The result is that a portion of the meristem becomes polyploid while the other may remain diploid. This would give rise to different types of chimeras depending on the nature of the layer or portion affected. If the chimera is of a periclinal nature (*i.e.*, a layer of one chromosome constitution encircling another), it is likely to be more stable. But if it is a mixo-chimera, where cells of different chromosome constitution are mixed without an apparent order, as growth advances branches of different constitutions or of a mixed constitution may be obtained. This would account for a large percentage of "reversion" we found in the branches developed from Agar-Colchicine treated buds. As the treatment itself would not have been so uniform as seeds immersed in Colchicine solution, the chances of differential action on the meristem are greater. It is possible that in such a case the mixed constitution would have continued for some time and later the diploid portion of the meristem assumed greater vigour at the expense of the Colchicine-affected polyploid portion. By the time flowers appeared only the diploid branches would have come up.

In a chromosomal chimera, the chimeral condition could not be propagated through the seed, as the embryo develops from a single fertilised egg and if subsequent nuclear divisions are regular, only an embryo with uniform chromosome number in all its cells would result. But as mentioned earlier, in a root-tip from the seed of a tetraploid (Figs. 18 and 18-a) we found a number of octoploid cells. The origin of this octoploid sector could be only due to a spontaneous doubling in one or more cells of the young embryo at a much earlier stage.

While chimeras of various types could be propagated vegetatively, the types of offspring produced by a chimera will depend on the chromosome constitution of the particular tissues from which the egg and pollen grain are formed. In flowering plants the layer immediately below the epidermis alone contributes to the formation of egg and pollen grains. So, in a chimera it is this layer which determines the character of an offspring. In a number of plants of *mug* in which the leaf epidermis was examined before the flowering stage, tetraploidy was expected on the basis of stomatal size, though pollen examination showed that in these cases the hypodermal layer was not affected. The work of Blakeslee and others have shown that periclinal chimeras could be easily induced by Colchicine. Due to the difference in chromosome number each germ layer could be distinguished and its contribution to the developing organs determined. The very interesting work of Satina, Blakeslee and Avery (1940) on the ontogeny of different organs in periclinal chimeras of *Datura* has already produced striking results and opened a new method of approach to an old problem. They have found that there are three independent germ layers in the shoot apex of *Datura*, the outermost corresponding to Hanstein's dermatogen, while the layer called periblem by him includes the second and third germ layers. The plerome is shown to be only a derivative of the third germ layer. This ability to label each germ layer separately has shown that the generally accepted notion that stamen is closely homologous with petal and leaf is erroneous. It may be expected that many problems in developmental morphology will be solved by a study of induced periclinal chimeras.

CONSEQUENCES OF AUTO-POLYPLOIDY

Polyploids, natural as well as artificial, are distinguishable from their diploid progenitors by the presence of *gigas* characters—thicker stem, greater vigour, thicker leaves with darker green pigmentation, and larger flowers and seeds. However, in Colchicine-induced polyploids, in the first generation, the plants are more stunted than the diploids. This is evidently due to some inhibiting effect of the drug. But it has been observed in a number of cases that in the second generation, the offspring from tetraploids show much greater vigour and are more hardy than diploids.

The doubling of the chromosome complement naturally means a doubling of the number of genes, though the genic balance remains unaltered. But the increase in cell size and nuclear size leads to various alterations in the physiological needs of the cell. The effect of this is manifested in a decreased growth rate in the tetraploid which consequently takes longer to reach maturity and the flowering stage than the diploids. Dobhzhansky (1937) has suggested a decreased rate of cell division as the most probable explanation of this difference. In discussing the relation between chromosome size and ploidy, Kostoff (1939) has pointed out that "smaller nuclei, typical for the diploids can be better supplied by the cytoplasm with substances necessary for the growth and reproduction of chromosomes than the large polyploid nuclei, since the former nuclei have larger surface in relation to their volume than the latter. The decrease of the ratio nucleus surface: nucleus volume (which he calls 'chromosome division co-efficient, "K," 1940) with the euploid increase of the chromosome numbers is probably the main factor that suppresses the frequency of the cell division in high polyploids." In a comparison of the root tip sections (see Figs. 13 and 14) we find that in the tetraploid, while the cells are larger, the number of cells is less than in the diploid. This supports the above suggestion of decreased rate of cell division with increase in ploidy and consequent decrease in "chromosome division co-efficient."

In chemical constitution also the tetraploids show many differences. Sansome and Zilva (1933) have found that tetraploid tomatoes have twice as much vitamin C as the diploid. Randolph and Hand (1938) found a tetraploid strain of maize to contain 43% more carotinoid per gram of dry meal than the corresponding diploid. This shows the possibility of increasing the nutritive value of plant products by doubling the chromosome number. In the present case we found an[illegible]crease in size of the seeds in the tetraploid (Fig. 17).

One of the important consequences of autopolyploidy is the formation of quadrivalents at meiosis leading to a certain percentage of unequal distribution of chromosomes in the resulting gametes. This would lead to a reduction in fertility, which is an important factor to be considered in crop plants grown for seeds. This disturbance does not occur in allopolyploids, which on that account have played a more constructive role in evolution. Kostoff (1939) from a study of chromosome behaviour in a number of polyploids has suggested that when autopolyploids are produced for practical purposes greater success may be expected from plants with a small number of small sized chromosomes, as in such cases the chances of quadrivalent formation in meiosis is considerably reduced. In *Phaseolus radiatus* the chromosomes are small and the number not high ($2n=22$) and hence regular meiosis may be expected in the auto-tetraploid. It may also be noted that natural autopolyploids in some species show greater physiological superiority and have proved to be even more successful than their diploid ancestors, in spite of the disadvantages resulting from irregularities in the chromosomal mechanism (Dobhzansky, 1937).

Now that we have a ready tool for inducing doubling of chromosomes, thanks to the work of Blakeslee and others, the next step is to find out how far the application of this discovery to crop plants would lead to results of economic importance. For this, many crop plants have to be investigated and the optimum treatment for each found out. A study of great importance would be to find out the differences in the physiological needs between the diploid and tetraploid under various controlled conditions. It would also be necessary to compare the yield as well as differences in chemical constitution. This is a vast field of enquiry and the co-operation of numerous investigators is necessary before we could achieve results of definite value.

SUMMARY

Artificial polyploidy has been induced in *Phaseolus radiatus* L. by Colchicine treatment. The technique adopted is described in detail.

Cytological examination showed the following chromosome numbers : $2n=22$; $4n=44$; $8n=88$.

Certain anatomical comparisons between the diploid and tetraploid are described.

The consequences of autopolyploidy, the importance of study of chromosomal chimeras and the lines on which further work on induction of polyploidy in crop plants have to be done are briefly discussed.

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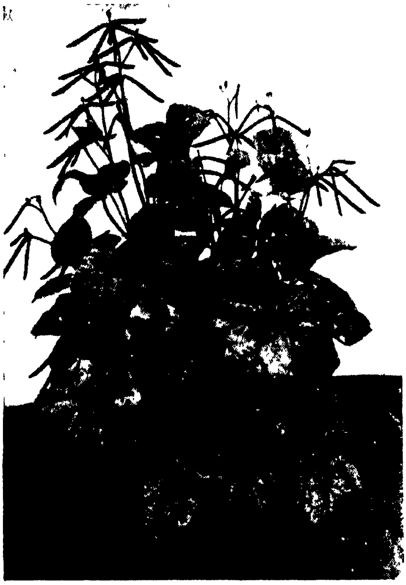
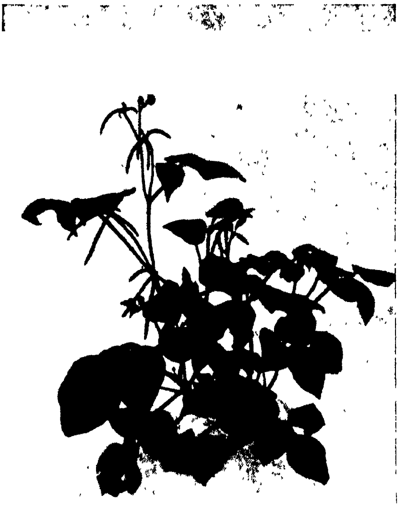


Fig. 1



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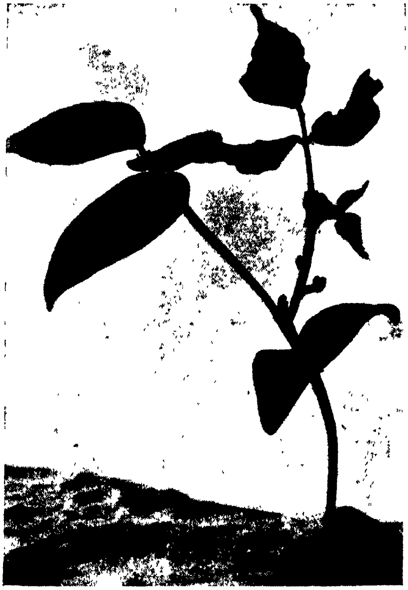

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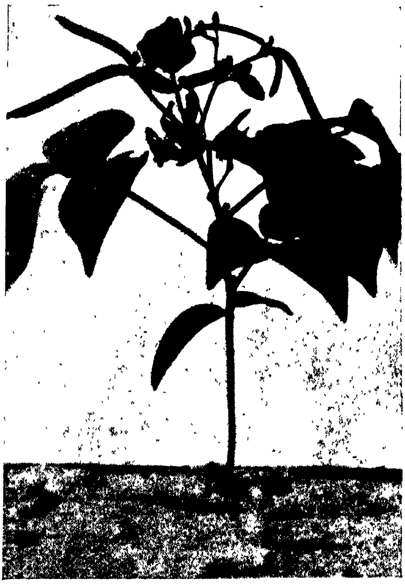
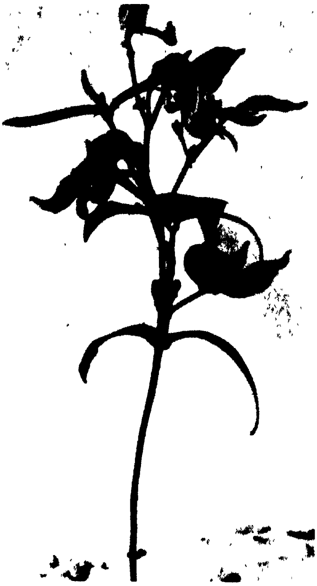


Fig. 4

Kumar and Abraham—Colchicine Polyploidy

Plate II



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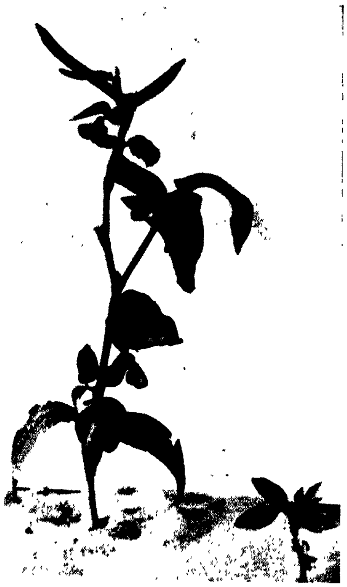

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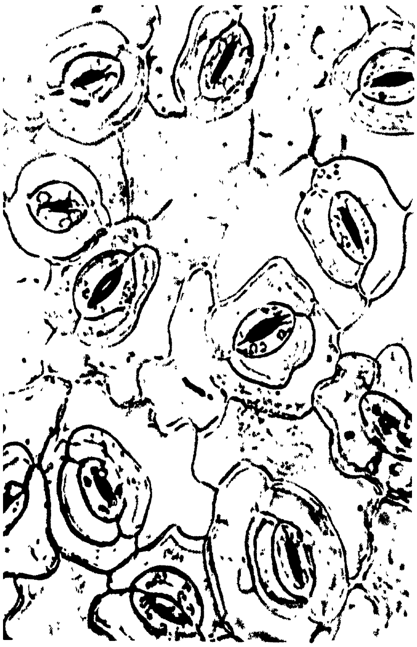

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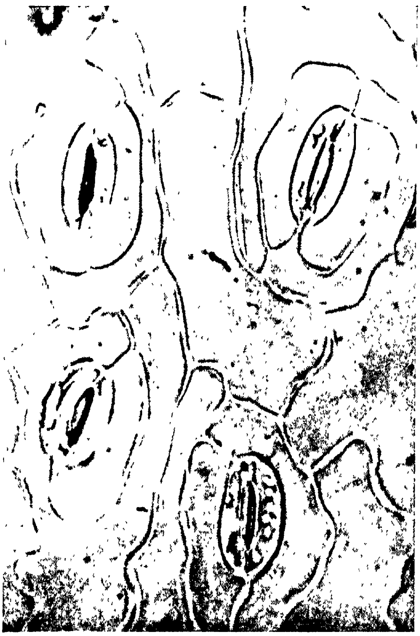

Fig. 8

Kumar and Abraham—Colchicine Polyploidy

PLATE III

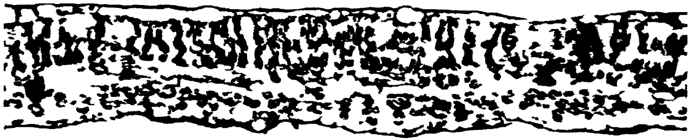

Fig 9

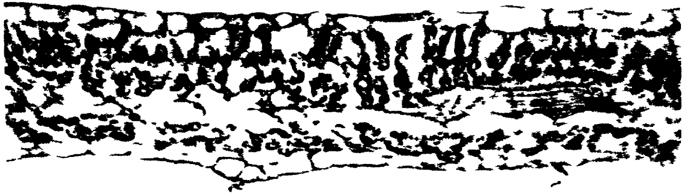

Fig. 10

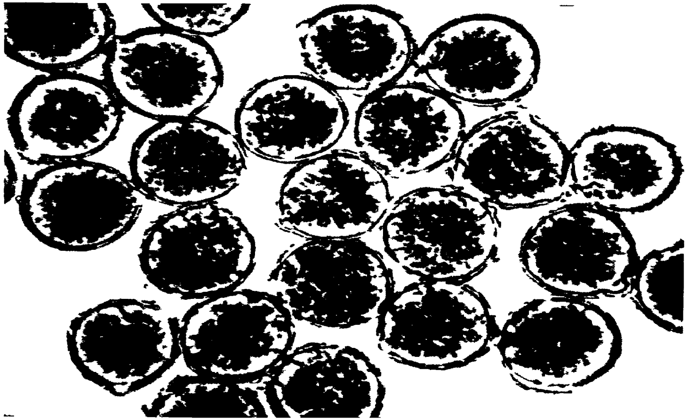

Fig 11

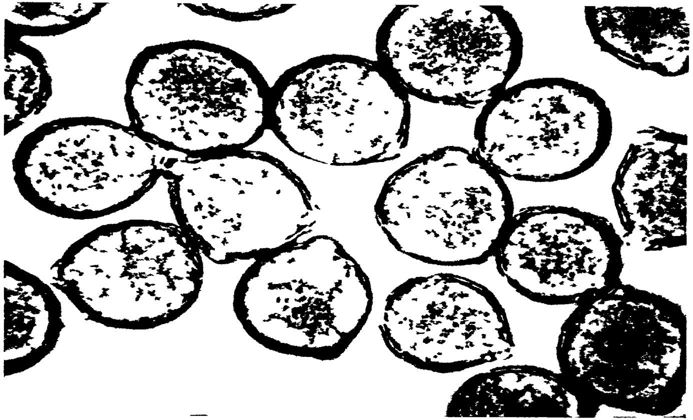

Fig 12

Kumar and Abraham—Colchicine Polyploidy

PLATE IV

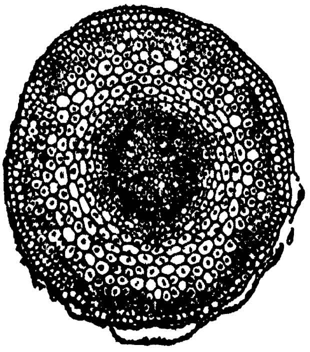

Fig 13

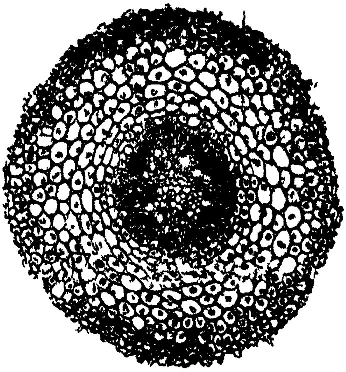

Fig 14

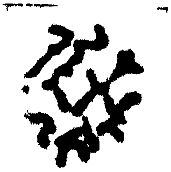

Fig 15

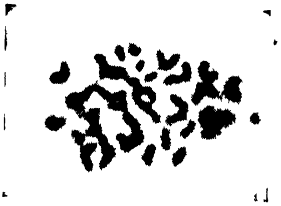

Fig 16

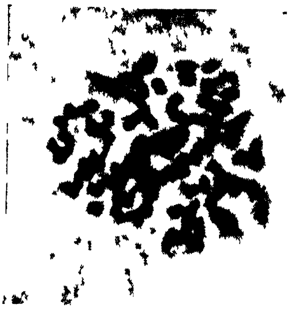

Fig 18

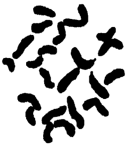

Fig 15a

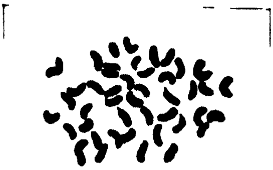

Fig 16a

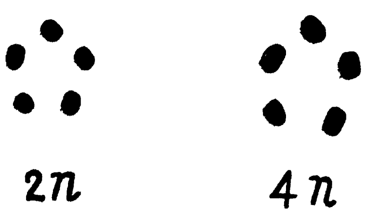

Fig. 17

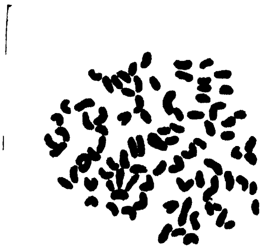

Fig. 18a

Kumar and Abraham—Colchicine Polyploidy

EXPLANATION OF PLATES I—IV

(Figures 1—6 are photographs of Phaseolus radiatus plants. All other figures, except Fig. 17, are photomicrographs of preparations made from treated and untreated mug plants. The magnification of each is noted after the legend)

PLATE I

Fig. 1—Photograph of untreated *mug* plant in the field showing the bushy growth.

Fig. 2—Plant which was treated with .05% Colchicine and grown in the field. Only one branch was tetraploid. Note stunted growth and smaller number of branches.

Fig. 3—Effect of Agar-Colchicine application to the terminal bud after the first compound leaf had developed. Compare the leaves before and after treatment.

Fig. 4—Untreated plant grown in pot.

PLATE II

Fig. 5—Tetraploid plant from Agar Colchicine treatment, grown in pot. Compare with previous photo.

Fig. 6—Another tetraploid plant from the same treatment as the above one. Note thick crinkled leaflets and presence of four leaflets instead of the usual three. The small plant on the right is also of the same age and shows the extreme stunting due to the drastic action of the drug.

Fig. 7—Lower epidermis of leaf of diploid control. × 540.

Fig. 8—Lower epidermis of strictly comparable leaf of induced tetraploid. Note increase in size in epidermal cells and stomata. × 540.

PLATE III

Fig. 9—Cross section of portion of a leaflet of diploid plant. × 120.

Fig. 10—Cross section of a comparable portion of the tetraploid. Note increase in size in all structures—epidermal cells, parenchyma cells, plastids, etc. × 120.

Fig. 11—Pollen grains (from flower just before opening) of the diploid; mounted in 50% acetic acid plus 50% glycerine to which a trace of iodine in potassium iodide was added. × 540.

Fig. 12—Pollen grains from tetraploid, collected from a flower of the same age and mounted in the same medium as the above. Note the increase in size of the grains, in thickness of the walls and in a few grains larger number of germ pores. × 540.

PLATE IV

Fig. 13—Cross section of a root tip taken from germinated seed of diploid control (Stained in gentian violet after hæmatoxylin). × 80.

Fig. 14—Cross section of root tip from germinated seed of tetraploid. The two sections have been selected on the basis of distance from the tip as determined by counts of number of serial sections from the tip section upwards. × 80. Note increase in size of cells and decrease in their number as compared with diploid.

Fig. 15—Chromosomes from root tip cell of the diploid (2n = 22). × 2400.

Fig. 15*a*—Indian Ink drawing made on a photomicrographic print to show more clearly the morphology of chromosomes which could not be brought out in photographing in one plane. Note presence of two satellited chromosomes.

Fig. 16—Chromosomes from root tip cell of the tetraploid (4n = 44). × 2400.

Fig. 16*a*—Similar drawing as 15*a* to show the number and morphology clearly.

Fig. 17—Photograph of seeds of diploid (2n) on the left and of tetraploid (4n) on the right. These seeds were taken from two pods both of which contained only five seeds each. (Natural size).

Fig. 18—Chromosomes at metaphase in a cell of the octoploid sector in a tetraploid root. Note that the chromosomes are smaller in size than either of the diploid or the tetraploid. × 2400.

Fig. 18*a*—Drawing on a photographic print to show clearly the number (8n = 88).

INVESTIGATIONS ON THE EFFECTS OF COLD STORAGE ON MOSAMBI (CITRUS SINENSIS)

By

G. S. CHEEMA, D.Sc., I.A.S.,

Horticulturist to Government, B. P., Poona,

AND

D. V. KARMARKAR, M.Sc., Ph.D., A.I.I.Sc.,

Senior Research Assistant, Cold Storage Research Scheme, Kirkee

INVESTIGATIONS on the 'storage life' of mosambi and subsequent changes in its composition in the cold storage throw a good deal of light on the possibilities of these results being commercially applied to mosambi trade.

It may be mentioned that mosambi is an important commercial fruit in Western India. It covers nearly 10,735 (1939-40) acres in the Province of Bombay alone. Citrus cultivation in Central Provinces, Western India, Madras and adjoining states covers approximately 80,000 acres. In spite of this, orange is imported into big centres like Bombay from Africa, Palestine and other sources. The imported orange is very popular on account of its brilliant attractive orange colour. It is only in the month of February that light orange coloured mosambi fruit is available in the Bombay market. The results of investigations, the details of which are given in this paper, show that mosambi fruit could be put in the market in fairly attractive condition to compete with the foreign fruit. Besides, the usual glut which is often experienced in the market in mosambi trade can be removed by adopting cold storage methods.

Cold storage trials of mosambi fruit were carried out at the Cold Storage Research Scheme, Kirkee, which is subsidized by the Imperial Council of Agricultural Research. The fruits required for the experimental trials were supplied by the Horticulturist to H.E.H. the Nizam's Government in 1938 and 1939.

PREVIOUS INVESTIGATIONS

Mosambi being a fruit of Western India and probably grown in some part of Africa, very little cold storage research is done on it. A good deal of investigation has been done on oranges in general in various countries. A review of literature on the cold storage of oranges in general by one of the authors is given in the Miscellaneous Bulletin No. 49 of 1942, published by the Imperial Council of Agricultural Research. It is, however, interesting to note here that Van der Plank and others[4] in South Africa have investigated that a temperature within the range of 50°-55°*F*. gave a good colour and almost all greenness of orange was removed. At 45°*F*. the colouring was very slow and at 39°*F*. there was hardly any colour. Leonard and Barker[3] have observed that green fruit ripened at 45°*F*. in storage. The ripe fruit lost its flavour and taste at this temperature. But it is not clear if the green fruit when it ripened developed orange colour. Chen[1] reports that thick skinned oranges with high acid and solid contents had better keeping qualities. This paper which exclusively deals with the storage life of mosambi gives prominence to the good effect of cold storage in regard to the development of colour and also the relation of storage to the quality of fruit in general.

EFFECT OF STORAGE ON THE DEVELOPMENT OF COLOUR AT DIFFERENT TEMPERATURES

Investigations show that the optimum temperature of storing mosambi is 40°*F*. At this temperature the fruit could be stored in saleable condition for four to five months. At 35°*F*. the fruit showed pitting of peel after a month's storage. At 40°*F*. the fruit slowly changed its colour and became yellow after four months of storage. The fruit developed uniform yellow colour after a month's storage at 52°*F*. and after two months it developed a bright orange colour and the fruit retained its fresh appearance. At this temperature an improvement in the colour of the juice was also noticed. Large fruit appeared to keep better than small fruit. At 68°*F*. the fruit changed colour after about a month but the skin wilted, the fruit became soft, and the juice gave fermenting odour.

In 1938 the fruit did not show any rotting during the first four or five months but in 1939 the fruits stored at 40°F. showed pitting of the skin after two months of storage.

CHANGES IN COMPOSITION DURING STORAGE

The percentages of pulp and peel, the juice content of the fruit, the specific gravity, solid content and acidity of the juice were determined after every month during storage at 52°*F*. and 40°*F*. Each sample consisted of ten fruits. The total weight of the sample was recorded. The fruits were then cut into halves and the juice was obtained by means of an ordinary lemon squeezer. The juice was filtered through thin muslin cloth and the total volume of the juice was measured. The "rag" from the pressed halves was carefully scraped out and the weight of the clean peel was obtained. The total weight of the fruit *minus* the weight of the peel was taken as equal to the weight of the pulp. The percentages of pulp and peel in the whole fruit were then calculated.

The quantity of juice per 100 gms. of fruit was calculated. The specific gravity of juice was determined at 68°*F.* by using a hydrometer. The solid content was determined by drying 10 cc. of the juice in a steam oven. The acidity was obtained by titrating 25 cc. of the juice sample with $\frac{N}{10}$ sodium hydroxide, using phenolphthalein as the indicator. The acidity has been expressed in terms of cc. of $\frac{N}{10}$ sodium hydroxide per 100 cc. of the juice.

The data obtained in the above analyses are given in Table I.

TABLE I

Change in Composition of Mosambi Orange during Storage at 52° and 40°F.

Period of storage in months	Percentage of pulp	Percentage of peel	Quantity of juice in cc. per 100 gms. fruit	Specific gravity of juice at 68°F.	Solid content in gms. per 100 cc. of juice	Acidity in terms of cc. of $\frac{N}{10}$NaOH per 100 cc. of juice
Fresh	75	25	43	1.034	8.01	31
Stored at 52°F.						
1	75	25	41	1.038	8.88	31
2	74	26	38	1.036	8.41	28
3	73	27	37	1.038	8.46	30
4	69	31	30	1.031	8.65	35
5	64	36	24	1.032	8.15	..
Stored at 40°F						
1	74	26	40	1.037	8.78	32
2	72	28	38	1.037	9.09	36
3	74	26	37	1.036	8.88	34
4	68	32	28	1.037	8.33	31
5	71	29	37	1.306	8.48	..

The data showed that the specific gravity, solid content and acidity did not show any marked change during storage either at 52° or at 40°*F.* The data showed that although the fruit stored at 52°*F.* for four and five months appeared to be quite fresh, it had lost its juice to a considerable extent.

LOSS IN WEIGHT DURING STORAGE

Two samples of ten fruits each of uniform size were kept in trays at 52° and 40°*F.* and the loss in weight was determined by weighing the samples every two weeks during the storage period. The results are given in Table II.

TABLE II

Loss in Weight of Mosambi Orange during Storage at 52° and 40°F.

Period of storage in weeks	Percentage loss in weight		Percentage loss at 52°F.: Percentage loss at 40°F.
	52°F	40°F.	
2	3.0	2.1	1.42
4	6.0	4.6	1.30
6	8.3	5.9	1.40
8	10.8	7.4	1.46
10	13.5	8.9	1.51
12	15.8	10.9	1.45
14	17.5	12.3	1.42
16	....	14.5	....

The increase in the percentage loss in weight at both the temperatures was steady and the ratio of the two percentages also did not show much variation. The external appearance of the fruit at both the temperatures was sound and there was no shrivelling of the peel. The greater loss in weight of fruit stored at 52°*F.* may be due to the partial desiccation of the pulp. It was noticed that in the fruit stored at 52°*F.* for four and five months, the pulp near the stem-end became considerably dried up, while in the fruit stored at 40°*F.* the pulp near the stem-end was only slightly affected after four months. It was found that in the fruit stored at 52°*F.* for four and five months the quantity of juice from the upper halves (stem-end side) was considerably less than that from the lower halves. The data are given in Table III.

TABLE III

Relative Juice Contents in Halves of Mosambi Fruit

	Quantity of juice per 100 gms. of fruit	
	Upper cc.	Lower cc.
4 months	23.8	34.6
5 months	18.4	29.1

It appeared possible that the loss of moisture from the pulp near the stem-end could be prevented by covering up the stem-end portion with vaseline or melted paraffin wax. Vaseline was applied to the stem-end portion of thirty fruits before storing them at 52°*F.* On examination of the fruit after four months of storage it was found that the application of vaseline was of no advantage as the pulp near the stem-end became as much desiccated as in the fruit stored without the vaseline treatment.

The losses in weight at 52°*F.* of the fruit with and without the vaseline treatment were determined and the results are given in Table IV. The ratio of the percentage loss in weight of the fruit without the vaseline treatment to the percentage loss in weight of the fruit treated with vaseline did not vary appreciably during the period of the experiment. Assuming that the difference between the two corresponding values was due to the loss in weight through the stem-end of untreated fruit, the value of this ratio indicated that only about one-eighth of the loss in weight occurred through the stem-end portion. Hence the application of vaseline to the stem-end portion did not appreciably reduce the loss of moisture from the pulp near the stem-end.

TABLE IV

Relative Loss in Weight of the Fruit With and Without the Application of Vaseline to the Stem-end Portion

Period of storage in weeks	Percentage loss in weight		Percent loss in fruit without vaseline : Percent loss in fruit with vaseline
	Without vaseline	With vaseline	
2	3.53	3.16	1.12
4	6.44	5.72	1.13
6	9.13	8.03	1.14
8	11.79	10.36	1.14
10	14.58	12.76	1.14
12	17.53	15.34	1.14
14	20.69	18.03	1.15
16	23.92	20.72	1.16

RELATION OF SIZE OF THE FRUIT TO ITS STORAGE BEHAVIOUR

During the storage trials in 1938 it was observed that at 52°*F.* the large fruit appeared to remain in a better condition than the small fruit after two months of storage when the small fruit began to get shrivelled and the appearance of the fruit became dull. It has been found by Karmarkar and Joshi[2] (1941, Ind. Journ. Agri. Sci., **10**, 1021-1029) that the loss in weight of small mosambi fruit was greater than that of large fruit. It was, however, noticed that large fruit lost more juice from the pulp than the small fruit. In 1939 two samples of large (weighing between 280 and 310 gms.) and small (weighing between 190 and 210 gms.) fruit, all individually weighed and numbered, were stored at 52°*F.* The percentage of pulp and peel were determined after 3 and 4½ months of storage. Ten fruits were first weighed (fresh weight) and then used for the analysis in each case. The data obtained are given in Table V.

TABLE V

Relative Changes in the Percentages of Pulp and Peel in Large and Small Mosambi Oranges during Storage at 52°F.

Period of Storage	Percentage loss in weight	Percentage of pulp		Percentage of peel	
		Fresh weight	Original weight	Fresh weight	Original. weight
		Large fruit			
Fresh ..	....	....	80.5	....	19.5
3 months ..	14.2	75.7	64.9	24.3	20.7
4½ months ..	22.9	74.6	57.6	25.4	19.6
		Small fruit			
Fresh ..	....	....	80.5	....	19.5
3 months ..	17.8	80.2	65.9	19.8	16.2
4½ months ..	26.8	79.3	58.1	20.7	15.4

The percentages of pulp and peel in the large and small fruits were equal in the fresh condition. The data showed that in the large fruit the percentage of peel, calculated on the original weight basis, did not show any significant change but it showed a considerable increase when calculated on the fresh weight basis. In the small fruit, on the other hand, the percentage of peel, calculated on the original weight basis, showed a definite decrease but it did not show any marked change when calculated on the fresh weight basis. The percentage of pulp in the large fruit showed a considerable decrease when calculated on the original weight basis and this decrease was approximately equal to the percentage loss in weight. This meant that the total loss in weight of the large fruit was entirely from the pulp and that the peel remained unaffected. In the small fruit the percentages of pulp and peel, calculated on the fresh weight basis, remained practically unaltered. The loss in weight took place proportionately both from the pulp and the peel. The difference in appearance between the large and the small fruits stored at 52°*F.* was, therefore, due to the fact that in the large fruit the peel remained unaffected during storage (except for the change of its colour) while in the small fruit it lost moisture, became shrivelled and appeared dull.

NATURE OF WASTAGE DURING STORAGE

During the 1938 storage trials practically no rotting was observed either at 52° or at 40°*F.* for four months of storage. During the 1939 storage experiments it was noticed that some of the fruit stored at 40°*F.* exhibited pitting around the stem-end after two months of storage. The fruit stored for a month at 52°*F.*, until it developed a good colour, and then transferred to 40°*F.* also showed pitting during storage at that temperature. The pitting appeared as sunken brown patches and, in the initial stages, was confined to the peel only, the pulp remaining unaffected. The fruit, however, lost its market value on account of the blemished appearance. On prolonged storage the pitted areas served as centres for the development of blue and green moulds and in the end the fruit rotted. At 52°*F.* the fruit was in a perfect sound condition and there was no blemish or wastage for three months. After this period a few fruits showed stem-end rotting. The portion of the peel around the stem-end first became soft, brown and watery and later blue and green moulds appeared. The total wastage on this account was about 10 per cent after four months of storage.

KEEPING QUALITY OF THE FRUIT AFTER REMOVAL FROM COLD STORAGE

Some fruits were removed after three months of storage at 52° and 40°*F*. and were kept at room temperature (70°-100°). A dozen fruits were packed in a small basket and kept in an experimental transport van. The fruits remained in good condition for four to six days. After a week the fruit kept at room temperature shrivelled, and the peel became tough and the juice gave a slightly fermenting odour.

SUMMARY

1. The results of the cold storage investigations on Mosambi fruit conducted in 1938 and 1939 at the Cold Storage Research Scheme, Kirkee, of the Imperial Council of Agricultural Research, are described.

2. Mosambi fruit which is usually of a pale yellow colour developed a nice orange colour after two months of storage at 52°*F*. At this temperature and at 40°*F*. the fruit could be kept in sound condition for 4-5 months, but in 1939 the fruit kept at 40°*F*. showed some pitting.

3. Determinations of the specific gravity, solid content and acidity of the juice did not show any marked change as a result of storage at 52° and 40°*F*. The data showed that although the fruit at 52°*F*. appeared quite fresh after four and five months of storage, it had lost its juice to a considerable extent.

4. At 52°*F*. the desiccation of the pulp was found to take place near the stem-end and the desiccation could not be stopped by applying vaseline to the stem-end portion.

5. The size of fruit was found to be very important in storage at 52°*F*. The data collected showed that in big fruits the peel remained unaffected and so the fruit appeared quite fresh, while in small fruit it lost moisture, the fruit shrivelled and appeared dull. The former lost more juice than the latter.

6. Fruit removed from cold storage after three months storage at 52° and 40°*F*. could remain in good condition for 4-6 days at ordinary room temperature.

ACKNOWLEDGMENT

The authors are greatly indebted to the Imperial Council of Agricultural Research for subsidizing the Cold Storage Research Scheme, Kirkee, where these cold storage investigations were conducted. They acknowledge the assistance rendered by Messrs. B. M. Joshi, R. K. Lavlekar and S. W. Rane in the experimental work.

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THE INFLUENCE OF CELLULOSE IN THE NITROGEN STATUS OF THE SOIL

By

REV. G. PALACIOS, S.J., Ph.D., D.D.,

AND

J. V. BHAT, M.Sc., Ph.D.

Microbiology Department, St. Xavier's College, Bombay

EMPIRICALLY it was found long ago that, to allow the stumps of crops to remain in the fields and then thereafter to plough these up so that they get intimately mixed with the upper layers of the soil, contributed considerably to maintain the fertility of the soil.

From scientific observations we find that denitrification in soil occurs in relation with the following four conditions:

(1) the presence of certain species of bacteria;

(2) a supply of nitrates;

(3) a considerable amount of easily assimilable organic matter;

(4) partial or complete anærobiosis.

The first condition mentioned above is established in the case of the so-called dry manures by the presence of straw which support an abundance of the denitrifying species of bacteria. It is a well known fact that denitrification is quite possible under anærobic conditions wherein ærobic organisms are active in removing the oxygen for their energy requirements from the nitrates and nitrites and that the amount of salts decomposed is proportional to the amount of assimilable carbon compounds available. By pot experiments it was observed by many workers that the addition of undecomposed farm-yard manure to soil resulted in the removal of nitrates. Similar results were obtained by the addition of chopped straw in large quantities to soils containing nitrates. Both of these bad effects were attributed to the presence of denitrifying bacteria which the dead organic material contained. At the same time it was found that well rotted dung, when ploughed into the soil, had no denitrifying effect, and so the conclusion drawn therefrom was that the factor responsible for denitrification was the undecomposed organic matter and not the denitrifying bacteria alone. Murray[4] on the other hand, has pointed out that the addition of straw, although it had a harmful effect on accumulated nitrates, did not cause a loss of Nitrogen to the soil as the actual estimation revealed. According to him, straw also acts as a source of energy for Nitrogen fixing bacteria, which seems obvious enough ; the amount of straw, however, does not in any way influence the amount of Nitrogen fixed.

Desai[8] also asserts that Nitrogen fixation does take place when straw or any other organic matter is added to the soil under favourable condition of temperature and moisture if sufficient time is allowed for their activity. Further proof of this statement is also afforded by other workers who have shown that the addition of the straw stimulated Nitrogen fixation in soil.

After the foregoing we presumed that the plant remains must have some definite and peculiar influence on the process of weathering. In our case the straw itself which deserved to be closely investigated had no special purpose to serve as we had to perform experiments with sterile series, and so we restricted ourselves to using pure cellulose (in the form of filter paper) to study its influence on the Nitrogen status of the soil.

EXPERIMENTAL

Apart from the control samples (for determining Nitrogen contents at the starting point) there were in all 72 experimental soil samples (5 grams each) contained in Erlenmeyer flasks provided with bacteriological cotton-wool plugs. These were divided into 2 series of 36 flasks each, and were tagged as the control series and the cellulose series. From each of the 2 series, 18 samples were sterilized and these constituted the "sterile set" and the remaining made up the "non-sterile set." Out of each of the two sets of both the series, 6 soil samples were rendered in a semi-saturated state by the addition of 3 cc. of sterile ammonia-free distilled water in each of them, and another group of 6 samples from every set was water-logged by the addition of 25 cc. of the same water aseptically. Then all the 72 soil samples were exposed in 3 groups to 3 different light-weather conditions, *viz.*, direct sunlight, diffuse sunlight and darkness for a period of 60 days. Then the Nitrogen contents, both total and soluble, of the specific samples were estimated by a standardised and modified Kjeldahl method; the values obtained for 5 grams of the soil were expressed as so many parts of Nitrogen per million parts of the soil.

The following tables will indicate the losses recorded in each of the differently treated samples of both the series under the 3 different light-weather exposures.

1. DIRECT SUNLIGHT

Losses in Nitrogen contents expressed in parts per million parts of the soil : The +sign before the figures indicates a gain *in Nitrogen*

Moisture condition of the soil	Soil without Cellulose				Soil with Cellulose			
	Non-sterile Set		Sterile Set		Non-sterile Set		Sterile Set	
	Tot. N	Sol. N	Tot. N	Sol. N	Tot. N	Sol. N	Tot. N	Sol. N
Dry	432.64	276.00	158.36	41.44	210.88	+4.40	172.28	4.00
Semi-saturated	398.72	258.88	189.32	20.72	415.80	+42.00	158.28	53.20
Water-logged	263.68	180.32	96.28	55.44	+668.92	+42.00	189.08	4.00

2. DIFFUSED SUNLIGHT

Losses in Nitrogen contents expressed in parts per million parts of the soil : The + sign before the figures indicates a gain *in Nitrogen*

Moisture condition of the soil	Soil without Cellulose				Soil with Cellulose			
	Non-Sterile Set		Sterile Set		Non-sterile Set		Sterile Set	
	Tot. N	Sol. N	Tot. N	Sol. N	Sol. N	Tot. N	Tot. N	Sol. N
Dry	1025.64	154.88	256.40	86.04	207.48	+9.20	130.40	0.00
Semi-saturated	432.64	62.94	78.44	41.44	137.48	56.00	159.00	+89.60
Water -logged	510.60	441.92	196.28	34.44	+622.12	+47.20	131.00	14.00

3. DARKNESS

Losses in Nitrogen contents expressed in parts per million parts of the soil : The + sign before the figures indicates a gain *in Nitrogen*

Moisture condition of the soil	Soil without Cellulose				Soil with Cellulose			
	Non-Sterile Set		Sterile Set		Non-Sterile Set		Sterile Set	
	Tot. N	Sol. N	Tot. N	Sol. N	Tot. N	Sol. N	Tot. N	Sol. N
Dry	277.20	138.88	107.16	20.72	114.28	19.60	65.80	+22.40
Semi-saturated	449.48	166.60	196.28	43.16	691.88	+2.80	187.00	14.00
Water-logged	474.08	258.88	189.32	23.36	691.88	86.80	205	14.00

The conclusions drawn regarding the influence of cellulose on the Nitrogen status (other conclusions have been stated in our previous article) are as follows :

1. The presence of cellulose definitely appears to have a protective influence on the status of Nitrogen in the soil as indicated by the smaller losses recorded for the Nitrogen contents of samples containing cellulose. Cellulose, in other words, retards the nitrogenous losses of both kinds—total Nitrogen and soluble Nitrogen—attributable to microbial and light-weather influences, except in the case of total Nitrogen samples exposed under darkness in a water-logged and semi-saturated states.

2. Under all light-weather conditions, the presence of cellulose in the soil is decidedly beneficial from the point of view of soluble Nitrogen content. In fact in many cases of non-sterile samples an increase in soluble Nitrogen content is observable.

3. Samples kept in water-logged state and exposed under direct sunlight and diffused sunlight show an enormous increase in both the total and soluble Nitrogen contents. This is clearly attributable to the Nitrogen fixation process that may take place under water-logged state in non-sterile samples.

4. Taking water soluble Nitrogen as a criterion of fertility, the presence of cellulose far from being in any way disadvantageous, actually improves the status of Nitrogen in the soil, and as such may be, in fact, a factor contributing to soil fertility.

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LOSSES IN SOIL NITROGEN CONTENTS

In Relation to Varying Periods of Exposure to Different Light-Weather Conditions

By

J. V. Bhat,

Microbiology Department, St. Xavier's College, Bombay

IN a previous article (Jour. Univ. Bom. Vol. X, Part 5, Sec. B, pp. 70-72) it was shown that the soil when exposed to diffused light suffers loss both in its total and soluble Nitrogen contents and that it is even possible to measure this daily rate of loss. It was further shown that the loss occurring during the first 24 hours of exposure is at its maximum and that thereafter there is a progressive decrease in the rate of loss of Nitrogen contents corresponding to the diminution in the total and soluble amounts of Nitrogen present in the soil. In this article an attempt is made to reveal the status of Nitrogen contents in soil samples when the samples were exposed to direct sunlight, diffused sunlight and darkness, under dry, semi-saturated and water-logged states, for exposure periods of 30, 60 and 100 days respectively.

Experimental

Apart from the control sets (for estimation of Nitrogen contents at the starting point) 108 Erlenmyer flasks, provided with bacteriological cotton plugs and each containing 5 gms. of the experimental soil samples (air dried and passed through a 20 mesh sieve) were taken; and 54 of them were sterilized by autoclaving for three days. The sterilized samples constituted the "sterile set" and the others constituted the "non-sterile set." Out of each of the two main sets 18 samples—sub-set—were meant for exposure to different light-weather, such as direct sunlight condition, for 30 days, another 18 samples for exposure for 60 days, and the remaining for a long exposure of 100 days, and they were marked accordingly. Out of each of the 18 samples meant for different periods of exposure from both the sets, 6 soil samples were rendered in a semi-saturated state by the addition of 3 cc. of sterile ammonia-free distilled water in each of them, and another series of 6 samples from every group were water-logged by the addition of 25 cc. of the same water aseptically. When the sets were ready the soil samples were exposed to direct light, diffuse light and darkness. One sub-set from each main set constituting a complete series of experimental samples, meant either for the exposure period of 30 days, 60 days or 100 days.

After exactly 30 days one series of experimental samples was taken and their Nitrogen contents—both total and water soluble—were estimated by the modified and standardised Kjeldahl method ; the values obtained for Nitrogen were expressed as so many parts of Nitrogen per million parts of the soil and these results were compared with those obtained for the soil samples analysed after 60 days and 100 days of exposure. The results obtained are mentioned in the following tables and the main conclusions drawn are discussed under each light-weather condition.

1. DIRECT SUNLIGHT : NON-STERILE SERIES

Losses in Nitrogen contents expressed in parts per million parts of the soil

Moisture condition of the soil	30 days exposure		60 days exposure		100 days exposure	
	Tot. N	Sol. N	Tot. N	Sol. N	Tot. N	Sol. N
Dry	398.72	180.32	432.64	276.00	449.48	318.92
Semi-saturated	360.36	204.32	398.72	258.88	432.64	318.92
Water-logged	220.76	166.60	263.68	180.32	280.04	204.32

2. DIRECT SUNLIGHT : STERILE SERIES

Moisture condition of the soil	30 days exposure		60 days exposure		100 days exposure	
	Tot. N	Sol. N	Tot. N	Sol. N	Tot. N	Sol. N
Dry	107.16	34.44	158.36	41.44	196.28	43.72
Semi-saturated	65.56	12.44	189.32	20.72	213.84	27.72
Water-logged	55.40	41.43	96.28	55.44	121.36	69.16

DISCUSSION

From the above two tables it becomes evident that the fall of the total Nitrogen in both the series (sterile and non-sterile) is the highest during the first 30 days of exposure, a little less in the next 30 days and still less in the next 40 days of exposure ; this indicates that the decrease in the rate of losses in Nitrogen keeps pace with the decrease in the Nitrogen quantity present in the soil. Or in other words the depleted soil seems to develop an increased retentive power as the total Nitrogen decreases. This is true in all the sterile series, the semi-saturated samples for total Nitrogen affording an exception in that in their case the highest loss in Nitrogen occurs during the next 30 days of exposure rather than during the first 30 days of exposure.

On comparing the losses in the non-sterile and the sterile series it will be noted that the losses occurring in the non-sterile series are in every case greater than the losses occurring in the sterile series, suggesting thereby the powerful depletory action of micro-organisms on the Nitrogen of the soil. It is also interesting to observe that the water-logged samples of both the series show a comparatively less depletion of total Nitrogen than do both the dry and the semi-saturated samples ; and it is equally interesting to note sterile samples showing greater losses in soluble Nitrogen which is probably attributable to the action of gases with water on Nitrogen contents.

3. Diffused Sunlight : Non-Sterile Series

Losses in Nitrogen contents expressed in parts per million parts of the soil

Moisture condition of the soil	30 days exposure		60 days exposure		100 days exposure	
	Tot. N	Sol. N	Tot. N	Sol. N	Tot. N	Sol. N
Dry	898.76	138.88	1025.64	154.88	1069.88	180.32
Semi-saturated	331.64	41.72	432.64	62.94	484.96	82.88
Water-logged	484.96	379.00	510.60	441.92	542.40	503.20

4. Diffused Sunlight : Sterile Series

Moisture condition of the soil	30 days exposure		60 days exposure		100 days exposure	
	Tot. N	Sol. N	Tot. N	Sol. N	Tot. N	Sol. N
Dry	190.32	69.16	256.40	86.04	290.32	93.16
Semi-saturated	52.42	27.72	78.44	41.44	107.16	43.72
Water-logged	134.88	27.72	196.28	34.44	238.76	41.44

Discussion

In this case the results obtained for the dry samples of both the series are conspicuous in that they are the highest losses recorded for both the total and the water soluble Nitrogen. In the non-sterile series, within 30 days an enormous loss in the total Nitrogen occurs, but during the next 30 days the loss that occurs is not even one-seventh of that recorded in the first 30 days. Further, if the losses recorded in the non-sterile series be compared with those obtained for the sterile samples, it becomes obvious that the action of micro-organisms on the soil Nitrogen contents is much more pronounced than that of the chemical agencies which are responsible for the losses in Nitrogen in the sterile samples.

Another interesting feature in the series is the huge losses observed in the non-sterile water-logged samples. These losses are clearly attributable to the denitrification process brought about in the soil by micro-organisms under anærobic conditions ; here the anærobiosis is provided by the water-logging, and the soil being in non-sterile state and under diffuse light the denitrification species could force their activities on the soil Nitrogen. This result corroborates those discussed in the article published in the last issue and dealing with the daily rate of loss in soil Nitrogen contents.

5. DARKNESS : NON-STERILE SERIES

Losses in Nitrogen contents expressed in parts per million parts of the soil

Moisture condition of the soil	30 days exposure		60 days exposure		100 days exposure	
	Tot. N	Sol. N	Tot. N	Sol. N	Tot. N	Sol. N
Dry ..	206.72	131.88	277.20	138.88	290.92	152.60
Semi-saturated ..	398.72	138.88	449.48	166.60	474.08	180.32
Water-logged ..	442.81	180.32	474.08	258.88	484.96	318.92

6. DARKNESS : STERILE SERIES

Moisture condition of the soil	30 days exposure		60 days exposure		100 days exposure	
	Tot. N	Sol. N	Tot. N	Sol. N	Tot. N	Sol. N
Dry ..	52.42	8.12	107.16	20.72	148.60	27.72
Semi-saturated ..	189.32	25.44	196.28	43.16	218.60	69.16
Water-logged ..	107.16	20.72	189.32	23.36	218.60	27.72

DISCUSSION

One important point in these results is the fact that contrary to the previous findings under direct sunlight and diffused sunlight, here greater losses are recorded in semi-saturated state of the soil than in the dry state ; so also in non-sterile samples the losses recorded under water-logged state are heavy. This is mainly due to the influence of the chemical agencies in both the series and this influence is bound to be more pronounced, as in this condition (darkness) the water, due to the relatively lower temperature of the samples, is likely to get more saturated with atmospheric gases bringing thereby greater losses in soil Nitrogen.

In other respects the general behaviour of the losses is at par with those recorded in all the cases, *viz.*, the greatest loss occurs during the first 30 days and thereafter there is a gradual decrease in the losses commensurate with the decrease in the amounts of Nitrogen present in the soil.

MAIN CONCLUSIONS

(1) Under all light-weather conditions, losses in soil Nitrogen contents occur more rapidly as a result of microbial action rather than that of chemical action as evidenced in the greater losses recorded in the non-sterile samples.

(2) In almost all cases the loss in Nitrogen was found to be at its peak during the first 30 days of exposure, and as a result of increased resistance of Nitrogen depleted soil to weathering, there is, thereafter a decreased rate of loss in Nitrogen.

(3) Although semi-saturation of the soil samples with moisture helps in the retention of soil Nitrogen contents under diffused light and direct light conditions, it works contrary when the samples are exposed to darkness.

(4) Maximum loss in total Nitrogen occurs in soil when the soil is exposed to diffused light in its air-dried state, whereas the maximum loss in soluble Nitrogen occurs when the soil is water-logged in the same light-weather condition.

EXTERNAL MORPHOLOGY AND ANATOMY OF SCORPION

(Buthus tamulus Fabr.)

By

V. B. TEMBE AND P. R. AWATI,

Royal Institute of Science, Bombay

INTRODUCTION

IN all the Indian Universities the scorpion is prescribed as a type of the class Arachnida for a detailed study. Most of the work on scorpions in India and abroad pertains to the pathology and biochemistry of their venom or to the taxonomy, ecology and distribution of these animals. Their general anatomy was first described by Muller in 1828 and by Blanchord in 1855 ; but their work was soon found to be inadequate by the later workers. So Huxley in 1859 studied the structure of its mouth and pharynx. Later on, Lankester and his co-workers described some of its systems in details. Povlovsky in 1927 has given a detailed description of the structure and ferments of its digestive system. Workers in India such as Mhaskar and Cauis have dealt with biochemistry of its venom. For a long time it has been found necessary to have a detailed anatomical work on an Indian scorpion. It is with this object in view that the present study was undertaken by the junior author at the suggestion of the senior author. The species Buthus tamulus Fabr. was selected for this work as it is commonly found in India. The investigation was carried out in the zoological laboratories of the Royal Institute of Science, Bombay.

EXTERNAL CHARACTERS

Buthus tamulus belongs to the family Buthidæ of the sub-class Scorpionidæ. The adult measures 65 to 90 mm. in length. The colour of the animal is variable. The dorsal surface of the body is blackish with a reddish or yellowish tinge, while the rest of the body is faint yellow. It is found throughout India except Malabar, Ceylon and Burma. The natural habitation of the animal is stony areas with sandy soil, generally on the slopes of hills.

It inhabits nooks and crevices under flat stones. It lives on maggots and insects by sucking their body fluids. It is found that they could be kept alive and quite healthy without food. In the laboratory they remained quite healthy even when kept without food for six months. It is a solitary animal but in the beginning of the monsoons we get females with 30 to 40 young ones living together. Scorpions are viviparous.

Its body is divided into three parts.The anterior portion of the body called the Prosoma is covered dorsally by a single shield, the carapace. It bears six pairs of appendages and of these the last four are its walking legs. The first pair consists of very small and short appendages called the chelicerae. They bear a strong contrast to the sensory antenna of insects. The second pair consists of long six-jointed pedipalps, which are grasping appendages. The rest of the body is distinctly segmented and differentiated into two portions: (*a*) the broad mesosoma or pre-abdomen consisting of seven segments of the same breadth as the prosoma and (*b*) the slender metasoma or post-abdomen consisting of five segments and a curved spine at the apex of which lie the openings of the poison glands. It is popularly known as its tail.

EXOSKELETON

The whole body of the animal is covered externally by a smooth or granular chitinous exoskeleton, often provided with short tactile hairs, which are generally longer on the legs and tail than on the trunk. On the segments of chelæ there are long and bristle-like hairs planted in circular integumental pits, known as setal, setiferous or bristle pores.

The prosoma is covered on the dorsal side by a single plate or shield known as the carapace (Fig. I,) It is formed by the welding together of six segments. It generally carries a median notch in its anterior margin thus forming right and left frontal lobes. In the middle of the carapace are situated two large median eyes (Fig. I, 3), while in the antero-lateral corners are placed two groups of lateral eyes (Fig. I, 1) each group consisting of three small eyes or eye-spots. Both kinds of the eyes are simple in nature. The part of the carapace between the lateral eye groups and the median eyes is termed the frontal area or ante-ocular triangle. In the genus Buthus the frontal area of the carapace is horizontal and there is no distinct transverse groove behind the eyes. The whole carapace is covered by granular crests or keels, which are distinguished as an anterior pair in front of the median eyes, a shorter median pair situated just behind the median eyes, and a longer posterior pair in the hind region. There is also a single lateral keel on each side. The whole carapace is finely and closely granular with more or less coarse granules on its sides and many on the anterior portion both between and outside the anterior keels. The ventral surface of the prosoma is covered by a small single median sternal plate (Fig. II, 4), which is triangular in form. It appears to be much reduced between the largely developed coxæ of the thoracic appendages, which almost meet each other in the median line. The carapace, the sternum and the appendages are bounded together by a chitinous membrane called the arthrodial membrane.

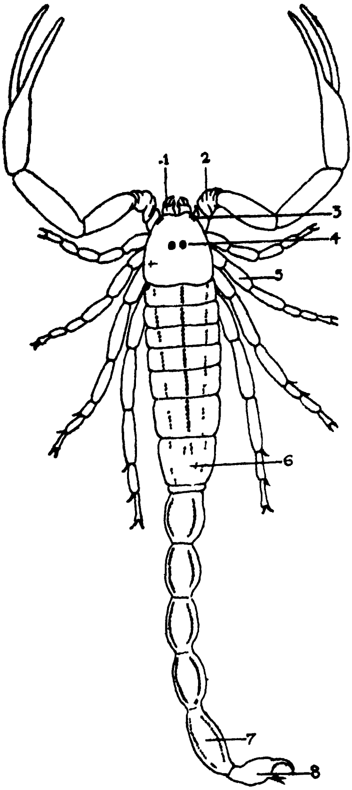


Fig. I. The dorsal view of the Scorpion.

1 Chelicerae, 2 Pedipalpi, 3 Lateral eyes, 4 Median pair of eyes, 5 2nd walking leg, 6 13th segment, 7 18th segment, 8 Telson, A Carapace (Prosoma), B—Mesosoma, C—Metasoma.

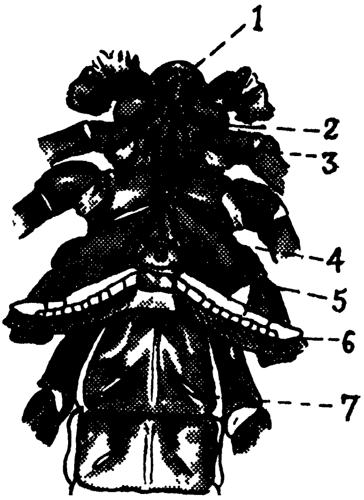


Fig. II. Ventral side of the scorpion showing from 1st to 10th segments. ×2.5.

1 Chelicerae, 2 Coxae of the pedipalpi, 3 Maxillary processes of the 2nd pair of legs showing gnathobases, 4 Triangular sternum, 5 Genital operculum, 6 Pectines, 7 Stigmata of the book-lung.

Behind the prosoma is the seven-segmented mesosoma. Each segment of it is covered dorsally by a tergal and ventrally by a sternal plate. The plates are as broad as the carapace. The terga and the sterna are joined to each other by their arthrodial membranes. In the seventh segment the tergum and sternum are narrowed and united posteriorly. Each tergum (Fig. I) bears on its surface a set of three keels, which may be smooth or granular, and the laterals of which are curved outwards at their anterior ends. The sternal plates are smooth, polished and light in colour. The sternum of the seventh abdominal segment is finely granular at the sides and carries four, nearly smooth or granular keels. The sterna of the third to the sixth abdominal segments possess each a pair of oblique slit-like stigmata (Fig. II, 7) situated laterally. On the inner side of the stigmata there are distinct muscular impressions. The second mesosomatic sternum is relatively small and is provided with a pair of peculiar comb-like appendages called the pectines (Fig. II, 6). They are considered to be the special organ of touch, a sense which is highly developed in scorpions. These enable them to determine the nature of things on which they are crawling. Pocock has seen a scorpion walk over a cockroach until its pectines came in contact with it, when it immediately backed itself and ate the insect. Each of these appendages consists of a handle or shaft and a series of movable teeth from 30 to 36 in number. The shaft consists of 3 segments. There are rounded chitinous pieces situated between the bases of the teeth and are called furcula. Anterior to the pectines, on the first sternum is situated the genital orifice, which is covered by a bifid movable lid, the genital operculum (Fig. II, 5).

Each of the five segments of the metasoma is enclosed in a complete chitinous ring. The first segment is wider than long, the second very slightly or scarcely longer than wide, the third one-fourth longer than wide, the fourth longer than the third and the fifth twice as long as wide. All these segments are granular and strongly keeled. According to their location they are designated as the superior median and the inferior median keels. Lateral to these are situated the superior lateral and inferior lateral keels. The keels on the sides are called the median lateral keels.

The metasoma ends in a post-anal sclerite called the telson (Fig. I, 8). This consists of two portions—a globular, swollen, proximal piece called the ampulla and a curved pointed claw like distal spine, the aculeus. In the ampulla is situated a pair of poison glands which open to the outside through a pair of openings borne near the tip of the curved aculeus. In the young stage of the scorpion the telson is very soft and whitish in colour, but as the animal grows older it becomes chitinised and grows darker. It has been proved by experiments that any injury to the telson, short of crushing, is easily and quickly repaired. If, however, it gets crushed, it simply dries and falls off, but its loss does not in any way affect the life of the scorpion, except perhaps serving it as a handicap in its struggle for existence.

External Apertures

The external openings of the body of the scorpion are as follows :

1. *Mouth* :—The mouth is a minute aperture situated at the hind end of the preoral cavity, situated at the anterior end of the body. The latter is on the ventral side of the medially placed soft rostrum and bounded laterally by the coaxæ of the pedipalps and ventrally by the maxillary appendages of the basal segments of the first and second pairs of legs.

2. *Anus* :—A median small aperture situated on the ventral surface between the telson and the last metasomal segment.

3. *Genital opening*:—It is a median opening situated ventrally on the first mesosomatic segment and is covered by the operculum.

4. *Stigmata* :—Four pairs of stigmata, each being situated laterally on the ventral surface of the mesosomatic segments from the third to the sixth, both inclusive.

5. *Openings of the poison glands* :—These are two small openings situated just behind the tip of the sting.

APPENDAGES

There are six pairs of appendages attached to the cephalothorax, which consist of a pair of cheliceræ, a pair of palpi, and four pairs of walking legs. The cheliceræ (Fig. III) are used to tear the hard integument of their prey. These appendages are homologous with the second pair of antennæ of Crustacea (Pocock). They are situated close together in the middle and project from beneath the anterior end of the carapace. They form the dorsal boundary of the preoral cavity in front of the rostrum. Each chelicera is formed of three segments (Fig. III). Its basal joint (5) is very small and triangular and is usually concealed beneath the carapace. The middle segment (4) is large and swollen and shows an angular surface which divides it into an inner and an outer side. At its distal inner end it gives off a strong procses bearing a set of teeth. This process is known as the immovable finger (2). On the inner inferior side of the segment there is a brush of long stout hairs called *dermato chætæ plerothæcatæ*, (3). The third segment of the chelicera is a small curved piece which constitutes the movable finger of the chelicera (1). This segment is produced into two fork-like processes each process having a set of teeth on its concave inner face which lies against the immovable finger. The movable finger works in a horizontal plane, so that the immovable finger fits in between the two processes of the former, thus forming a chela when brought together.

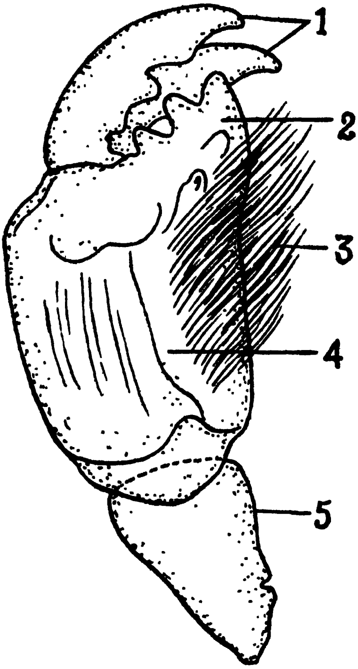


FIG. III. Chelicera. ×40.

1 Movable finger of the chelicera, 2 Immovable finger, 3 dermato-chætæ plerothaecatac, 4 2nd segment, 5 Basal segment.

The Pedipalpi : (Figs. IV and V). The second pair of appendages is known as the pedipalpi (chelæ). They form an efficient weapon of attack for the scorpion. They are pincer-like in form, and move almost in a horizontal plane. Each pedipalp is formed of six segments which counting from the basal one, are the coxa, trochanter, humerus, brachium, hand and movable finger. The coxa (7) is situated on the side of the preoral cavity beneath the carapace. It is freely movable with its inner surface and works as a jaw. It is used in compressing its prey and squeezing out its body fluid. Its concave median surface is usually provided with a dense hairy cushion of soft chitin. The edges of this surface are sharply ridged and covered with thick setæ. The second segment, the trochanter (6) is strongly chitinised, cubical in form and shows many crests. The humerus (5) and brachium (4) are almost equal in size. They are more than double the length of the trochanter, and are furnished with granular keels. The humerus is set at right angle to the long axis of the body, while the brachium and the hand are located in a line parallel to the long axis of the body. The humerus has thus an anterior and a posterior surface, whereas the brachium and the hand have each an outer and an inner surface. At the outer and anterior end of the humerus and at the posterior end of the brachium on its inner surface there is seen a concave depression to the inner side of which are inserted strong muscle bands. This helps the animal to move the brachium inwards in a horizontal plane. At the anterior end of the brachium there are outer and inner depressions formed by the overgrowth of upper and lower edges. Thus a socket is formed in which fits the projection of the posterior end of the hand. The hand can freely move inwards or outwards in a horizontal plane. The brachium is broader than the humerus.

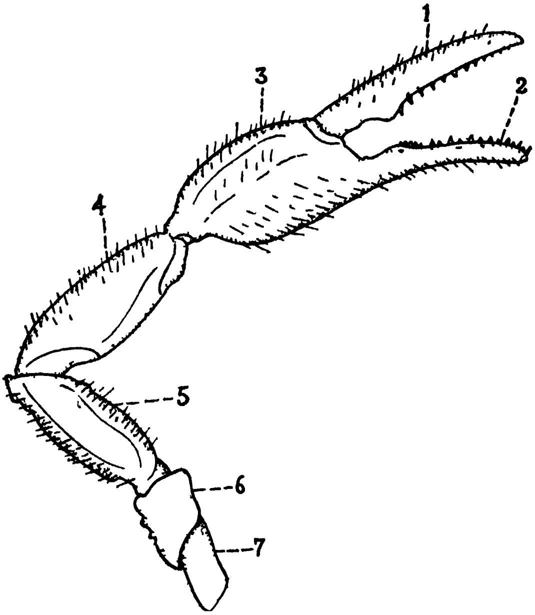


FIG. IV. Pedipalp (chela) ×16.
1 Movable finger, 2 Immovable finger, 3 Hand, 4 Brachium, 5 Humerus, 6 Trochanter, 7 Coxa.

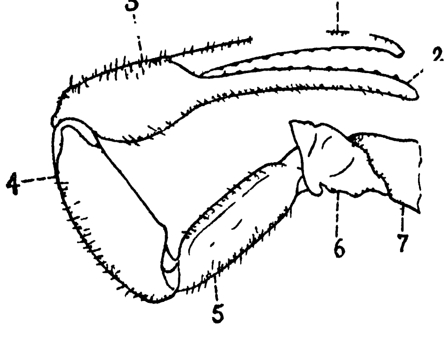


FIG. V. Pedipalp of a female Scorpion (Chela)

The hand of the scorpion shows variations in form in different sexes and species. In the male it is strong, short and globular at its base (Fig. IV), while in the female it is rather long and slim (Fig. V). Along its outer and lower side is attached the last joint of the chela known as the movable finger (1). The surface of the hand that lies just behind the joint of the movable finger is flat and rests upon the ground. This portion is called the under-hand and is separated from the upper side of the hand by the growth of a keel. The upper side is generally evenly convex in this species. There are some faint keels developed on the upper-hand also. The keel stretching from the immovable finger (2) to the base of the hand is known as the finger keel. The fingers are provided with teeth on their grasping surfaces. The arrangement of these teeth is useful and found to be of taxonomic importance. (Fig. VI). There are several rows of small teeth, running obliquely and close together. These rows form the median series of teeth (1). The anterior tooth of each row of the median series, is often enlarged and distinguished by its size. These enlarged anterior teeth form the inner series. Similarly the two posterior teeth of each row are also enlarged and form an outer series.

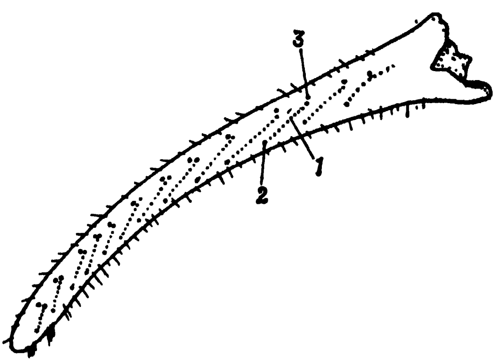


FIG. VI. Movable finger of the scorpion. ×8.
1 Medium row of teeth, 2 Anterior tooth, 3 Posterior tooth.

Neither the chelicerӕ nor the coxӕ of the pedipalpi bear any glands. In this respect the scorpions differ markedly from the spiders the chelicerӕ of which enclose the poison glands, and the basal joints of the maxillӕ of which contain the salivary glands (Pavlosky)^{8}.

Legs :—There are four pairs of legs which are structurally alike and are used for walking. They are attached to the body at the sides of the cephalothorax. Each leg (Fig. VII) consists of seven segments which beginning from the proximal one, are coxa, trochanter, femur, patella, tibia protarsus and tarsus. The tarsus bears at its tip two or three claws.

The coxӕ of the first and second pairs of legs are each provided with a triangular process directed forward, and lying immediately below the mouth. It is known as the maxillary appendage (Figs. II and X). These maxillary appendages form the floor of the preoral cavity. On the upper surface of the first pair of maxillary appendages there are numerous dense hairs. The coxӕ of the second pair of legs meet each other in the middle line. Their upper and lateral parts are covered with soft chitin bearing numerous dense hairs called *dermatochælæ anthæchct.* Each appendage has a longitudinal groove on the superiolateral surface. The coxӕ of the 3rd and 4th legs of each side are fused together and are separated from those of the opposite side by the sternum of the prosoma or cephalothorax (Fig. II) which abuts anteriorly against the coxæ of the 2nd pair.

To the distal end of the coxa is articulated the trochanter (Fig. VII, 2) which is very short and stout. It moves in backward-upward and downward-forward directions. The third segment, the femur (3), is straight and long and moves very freely upwards and a little sideways ; while the next segment, the patella (4), moves downwards freely. The tibia and the protarsus show a downward bending, but the tarsus can move freely in all directions. At the distal end of the tibia where it articulates with the protarsus, is seen a pale and dark-tipped claw-like spur known as the tibial spur. Such spurs are found on the 3rd and 4th legs. Similarly there is a pair of pedal spurs at the extremity of protarsus where it joins the tarsus. The anterior one of the pedal spurs is often double being furnished with a branch. On the lower side of the tarsus there are two rows of spinules. At the distal end of the tarsus are articulated the three claw, of which two are superior and one inferior, the latter being often partially or wholly worn down. At this end of tarsus is produced into a small flap called the claw-lobe.

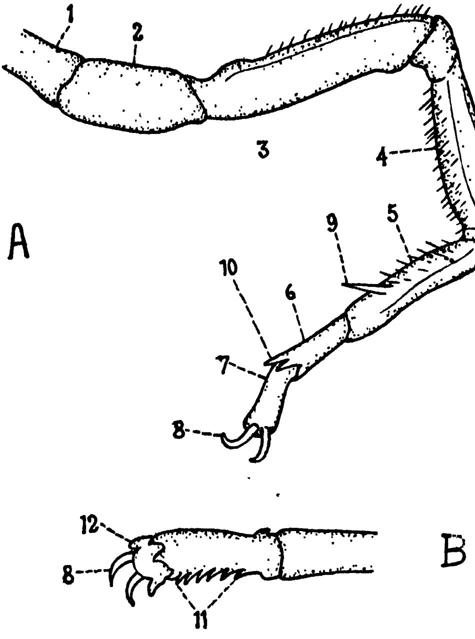


FIG. VII. A walking leg of the scorpion.

1 Coxa, 2 Trochanter, 3 Femur, 4 Patella, 5 Tibia, 6 Protarsus, 7 Tarsus, 8 Claw 9 Tibial spurs, 10 Pedal spur, 11 Row of spinules, 12 Lateral lobe overlapping the base of the claw.

B—Side view of the tarsus.

THE INTEGUMENT

The body-wall is characterized by its assumption of both protecting and supporting functions. It consists of three main layers the outer-most of which is formed by the cuticle, a non-cellular substance of a secretory nature. Beneath the cuticle lies a layer of cubical epithelium known *as the hypodermis. At different spots the cells of the hypodermis are modified into hair-producing cells called trichogen* (Comstock[18]), the body of which sinks below the hypodermal level. The shaft of the hair rises through the hypodermis and pierces the cuticle, the latter forming the trichopore. The third and innermost layer is made up of apparently structureless membrane forming what is known as the basement membrane which lines the inner side of the hypodermis.

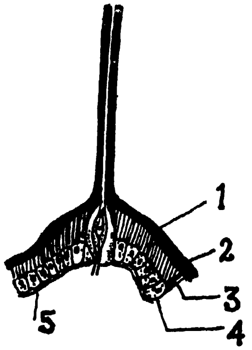


FIG. VIII. Body-wall of the scorpion with the hair. ×120.

1 Testostracum, 2 Epiostracum, 3 Hypostracum, 4 Hypodermis, 5 Basement membrane.

The cuticle (chitin) is a nitrogenous organic compound belonging to the scleroprotein group of the poly-peptides (Savory). It is not much affected by ordinary reagents such as dilute alkalies or acids and so it very well serves as a protective covering for the animal. If the body of the scorpion is boiled in dilute caustic potash solution for about an hour, the whole of the internal tissues get dissolved and only the chitinous exoskeleton is left behind as a hollow case. The colour of the chitin can be bleached by an oxidising agent.

Microscopical examination reveals that the chitin is formed of several layers consisting of the following parts (E. N. Povlovsky[8]), (1) a superficial cuticular layer known as Testostracum (2) the middle layer called Epiostracum and (3) the deep lamellous layer—the Hypostracum, In the chitin there are two types of canals of which one type is situated in the hard region of the integument. This canal is smoothwalled and reaches the very surface of the chitin. Its lumen is occupied by protoplasmic material containing rod-shaped nuclei and pigment granules. The other canal is broader and is found in the softer parts of the integument (the pleura of scorpion). The walls of this canal are supported by circular thickenings (rings). It appears to perforate the chitin. From its apex short chitinous tubules run inwards.

The sculptures on the integument is of two types: (1) dermatidia, which are formed only by the dermal lining (chitin, hypoderm, basement membrane), (2) cælodermidia which are provided with an cavity which is the continuation of the body-cavity. The latter includes the different outgrowths of the integument, e.g., the cristæ, tarsal claws, spines of the claws, spurs, etc. To the former belongs the chætoids, *e.g.*, denticles on chelæ, sculptured processes on the posterior margin of stigmata, etc.

THE DIAPHRAGM AND THE ENDOSKELETON

Like the exoskeleton there are also some internal skeletal structures used generally for the attachment of muscles.

On removing the carapace of the cephalothorax and the tergum of the seventh segment it is found that the prosoma is separated from the mesosoma by a chitinous and muscular wall called the diaphragm (Fig. IX, *b*). A close examination shows that the diaphragm is formed by a strong intucking of the intersegmental membrane between the 6th and 7th segments, so that it is composed partly of a chitinous infolding and partly of muscle bands. It seems that the opposite inter segmental intuckings fuse together to form a diaphragm (Bernard). The dorsal blood vessel, the alimentary canal and the nerve cord pierce through it. In front of the diaphragm there is a chitinous plate situated dorsally to the nerve cord and ventrally to the alimentary canal. This plate is the endosternite. It is a complicated structure because the strong longitudinal compression of the thorax has caused it to fuse posteriorly with the diaphragm (Bernard). The endosternite has got many processes to which muscles from different directions are attached. It fuses with the diaphragm at four points. (1) The postero-lateral tendons of endosternite fuse with the ridges of the diaphragm which are caused by the dorso-ventral muscles behind it, the muscles being secondarily attached to the endosternite afterwards. (2) The horizontal plate of the endosternite is attached to the anterior face of the diaphragm by two processes.

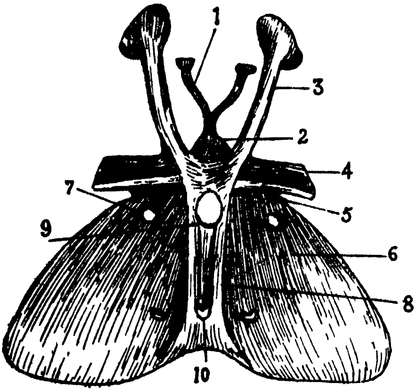


FIG. IX. Endosternum of the scorpion. Dorsal surface.

1 Paired anterior process of the subneural arch, 2 Subneural arch, 3 Anterior lateral process, 4 Lateral medium process, 5 Posterior process, 4 Lateral medium process, 5Posterior process, 6 Posterior flap or diaphragm, 7 Perforation of the diaphragm for the passage of muscles, 8 The paired dorsal ridge, 9 Gastric canal or foramen, 10 Arterial foramen.

Histologically the endosternite is formed of apodomes (internal prominences of the chitin for muscle attachments) and owes its origin to the fusion and longitudinal compression of the cephalothoraic segments. Afterwards it becomes almost entirely detached from the parent cuticle. By fusion of the endosternite with the diaphragm the scorpion does not retain the original condition of the arachnidian thorax. This fusion has misled investigators into believing that the endosternite and the diaphragm belong to one another as parts of one and the same structure.

THE DIGESTIVE SYSTEM

The alimentary canal is a tube extending from the mouth to the anus in a straight line. It is distinguishable into four principal regions (1) The pre-oral cavity, (2) The four-gut or stomodæum, (3) The mid-gut or mesenteron, and (4) The hind-gut on proctodæum.

THE PRE-ORAL CAVITY

It is enclosed by the basal segments of the anterior four pairs of appendages. Dorsally the cavity is bounded by those of the chelicerae (Fig. X); laterally it is limited by the coxac of the pedipalps (3) and ventrally it is supported by the two pairs of maxillary appendages of the first two pairs of legs (5 and 6). All these segments are covered on their inner surfaces, with bristles. There protrudes a custion-like structure from the posterior surface of the pre-oral cavity. It is ventrally elevated and laterally compressed and is known as the Rostrum (2). Dorsally it is broad and rounded with a slight median ridge. Its lateral surfaces are oblique, while the ventral edge is convex. Postero-anteriorly it is narrowed. It is covered all over its surface by soft hairs, which resemble those that are found on the pedipalpal cushions. (M. Blanchard has named the rostrum as "Buccal appendages"). Its dorsal ridge fits in a corresponding furrow between the chelicerae. As observed by Pavlovsky, the folds of the teguments on its dorsal and lateral surfaces are not glandular. The transverse section of the rostrum shows that there are several muscle-bands inside (Figs. XI and XII).

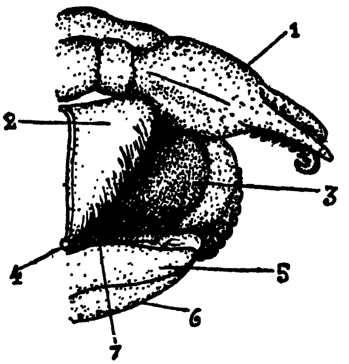


FIG. X. Side view of the preoral cavity. The chelicerae and the pedipalps of the right side have been completely removed.

1 Left chelicera, 2 Rostrum, 3 Coxa of the left pedipalp, 4 Mouth opening, 5 and 6, Maxillary appendages of the 1st and 2nd walking legs 7 Preoral cavity.

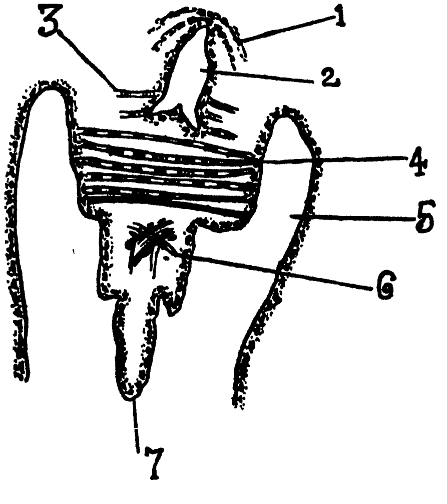


FIG. XI. Horizontal section through the rostrum and pharyngeal sucking apparatus.

1 m. sphincter pharyngeales 2 Pharynx, 3 m. rostropharyngeales inferior lateralis 4 m. transversus rostri 5 Pedipalps, 6 transversus rostri obliquus 7 Rostrum.

The latter may be divided into two groups: (1) the proper rostral muscles and (2) the rostropharyngeal muscles connecting the rostrum to the pharynx. To the first groups belong (*a*) m. transversus rostri maximus, (*b*) m. transversus rostri diffurus, and (*c*) m. obliques rostri ventralis. When the first two muscles contract the rostrum is compressed. When the last paired muscles contract the ventral half of the rostrum is contracted and in this way allow a wider passage to the oral opening. The rostropharyngeal muscles consist of (*a*) m.m. rostropharyngeales superiores which are extended from the pharnyx to the upper wall of the rostrum, (*b*) m.m. rostro pharyngeales inferiores mediales attached from the lower part of the rostrum to the pharynx. These muscles help to dilate the pharnyx and also to draw backwards, upwards and inwards the inferior surface of the rostrum.

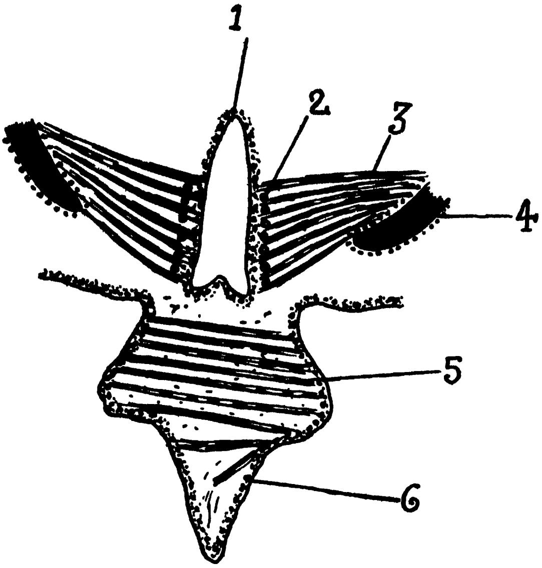


FIG. XII. Horizontal section through the ends of the preoral entosclerite.
1 Pharynx, 2 m. sphincter pharyngis, 3 m. dilatator pharyngis lateralis 4 Part of the preoral entosclerite, 5 m. transversus rostri 6 Rostrum.

FOREGUT OR STOMODAEUM

The foregut (Fig. XIII) consists of (*a*) the mouth opening, (*b*) the pharnyx with the sucking apparatus (*c*) the œsophagus and (*d*) the post-cerebral sucking apparatus.

The mouth :—The mouth, as already mentioned, is situated below the base of the rostrum surrounded by the maxillary appendages of the first pair of legs and the adjoining parts of the coxal joints of the pedipalps.

The pharynx:—The mouth leads into the pharynx (Fig. XIII, 8) which is dilated and modified into a sucking chamber. It is situated between the rostrum (3) and the anterior portion of the cerebral ganglion (9). In the longitudinal section it appears somewhat pear-shaped, with its broader end being uppermost and its longer axis directed diagonally backwards. Its broad upper end lies between the two anterior processes of the endosternite. It is lined on its inner surface with a thick chitinous intima. Its epithelial cells (14) lie in a layer underneath the cuticle. It is provided with numerous muscles (7) on its outersurface. They enable the pharynx to suck juices. These muscles can be divided into two groups (Povlovsky 10): (1) dilatators and (2) sphincters. To the former are referred (*i*) m. dilatator pharyngis lateralis (Fig. XII 3) from the lateral walls of the pharynx to the processes of thr pre-oral endosclerite, (*ii*) mm. rostropharyngeales inferiore, (*iii*) m.m. rostropharyn geales superiores, (*iv*) m. dilatator pharyngis suprarostralis inferior from the pharynx to a point above the base of the rostrum and (*v*)m. dilatator pharyngis suprarostralis superior (Fig. XIII) a paired muscle bands extending from the upper part of the pharynx to the anterior end of the cephalothorax. The sphincters of the pharynx consist of the muscle bundles surrounding the pharynx and alternating with the bundles of dilator muscles.

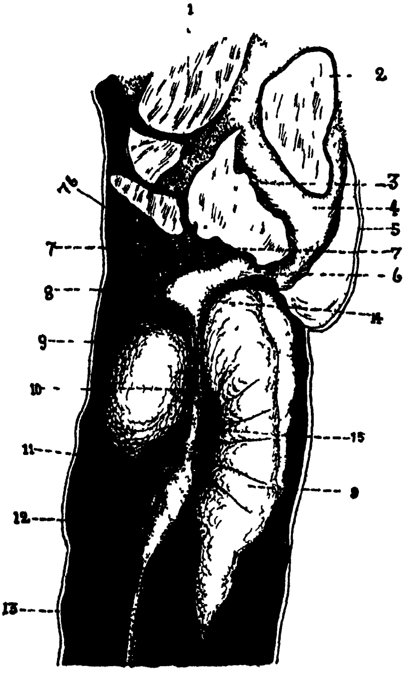


Fig XIII. Longitudinal section of a young scorpion going through the alimentary canal.

1 Distal joint of the chelicera, 2 Portion of the coxa of a pedipalp, 3 Rostrum, 4 Preoral cavity, 5 Maxillary appendage of the legs, 6 Mouth, 7 Muscles of the sucking apparatus of pharynx, 8 Pharynx, 9 Portion of the brain, 10 Oesophagus, 11 Oesophageal valve 12 Stomach, 13 Intestine, 14 Epithelial layer of pharynx covered by a thin chitin, 15 Connective Tissue, 7a and 7b M dilatator pharyngis subrostralis interior 7c M dilatator pharyngis suprarostralis superior

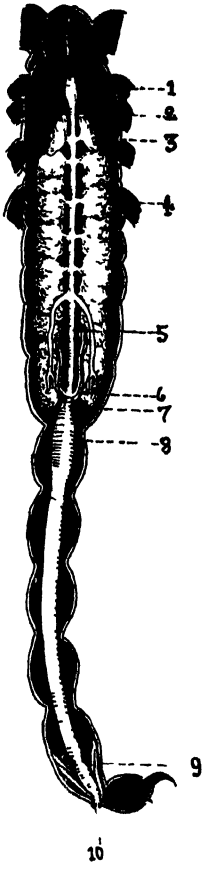


Fig XIV Digestive system of the scorpion.

1 Pharynx, 2 Oesophagus, 3 Stomach gland, 4 Hepatic gland, 5 Pars tecta intestini, 6 Malpighian tubules, 7 Constriction of the intestine, 8 Pars nuda intestini, 9 m Levator ani, 10 Anus.

The Œsophagus :—The pharynx leads into the œsophagus (Fig. XIII, 10) which is a thin, delicate and narrow tube. It passes through the cephalic nerve ring. Owing to the presence of the longitudinal folds in its wall its lumen appears to be stellate (Fig. XV). In the transverse section it appears to be formed of the following layers from outside inwards; (1) membrane externa, (2) membrane propria, (3) epithelial layer covered by (4) chitin. Posteriorly the epithelium widens.

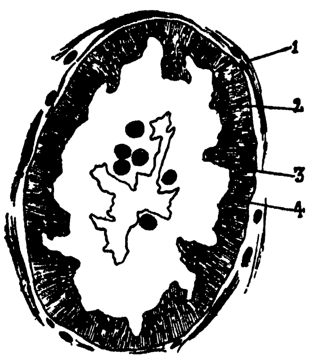


FIG. XV. Transverse section of a young scorpion passing through the intracerebral portion of the oesophagus.

1 Membrana externa, 2 Membrana propria, 3 Epithelium, 4 Chitinous layer.

In the muscular layer there are longitudinal fibres which act to strengthen the œsophageal walls. At the postcerebral side of the œsophagus the *epithelial layer* shows a thickening which is more on the dorsal side of the lumen, thus forming a type of a valvular structure. (Fig. XIII). The latter might be useful in preventing the return flow of the stomach contents.

THE POST CEREBRAL SUCKING APPARATUS

The post-cerebral sucking apparatus consists of the muscle-band called (*i*) m.m. dilatators œsophagi retrocerebrales laterales, extendi- from the post cerebral portion of the œsophagus to the anterior processe of the endosternite and (*ii*) m.m. dilatators œsophagi restrocerebrale radiales extending from the lateral and superior surfaces on the œsophagus to the sides where they are lost between the lobules of the digestive glands. The sphincters of this sucking apparatus are in the form of circular muscle fibres.

THE MIDGUT OR MESENTERON

The midgut is formed of (*a*) stomach, (*b*) intestine with the two digestive glands: *viz.*, (*c*) stomach gland and (*d*) hepatopancreas.

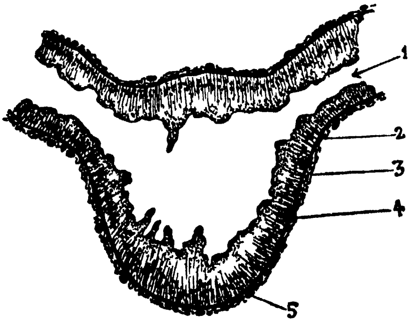


FIG. XVI. T. S. of the stomach where the stomach glands open into it.

1 Opening of the stomach gland, 2 Membrana propria, 3 Muscles, 4 Epithelium. 5 Longitudinal muscles,

(*a*) The stomach is the dilated portion extending from the œsophagus to the diaphragm and situated in the cephalothorax. It is easily distinguishable from the œsophagus by the absence of the chitinous lining in the lumen. It is covered dorsally and laterally by a brownish gland called the stomach gland (Pavlovsky). The gland is trilobed : a median dorsal and two lateral lobes. It has two ducts which enter the stomach.

The transverse section of the stomach shows that it is lined inside with a cylindrical epithelium. The epithelium consists of two kinds of cells, *viz.*, the absorbing cells irregularly alternat'ng with the ferment cells. The epithelium is based on the membrana propria.

(*b*) The intestine is the longest portion of the alimentary canal which occupies the pre-and post-abdominal region. It is distinguished into two parts by the presence of a circular constriction in the region of the 13th segment (Fig. XIV) from where two pairs of small malpighian tubules are given off. Its anterior portion is the hepatopancreatic portion and is called the *pars-tecta intestini*. It is not as broad as the posterior part and occupies almost the whole length of the preabdomen. It gives on each side five narrow ducts which lead into the substance of the large heptopancreas,which occupies the whole cavity of the preabdomen. The microscopical study of the parstecta intestini (Fig. XVII) shows that the epithelial cells are glandular resembling the heptopancreatic cells.

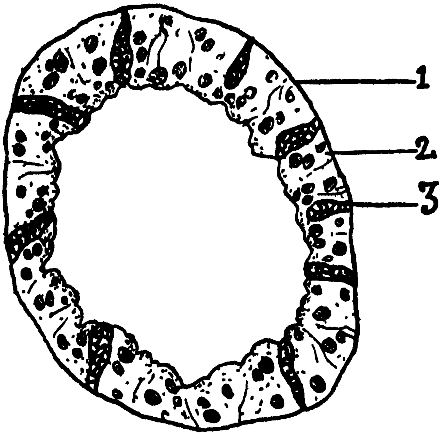


FIG. XVII. T. S. of the pars tecta intestini. 1 Membrana propria, 2 Absorbing cells, 3 Ferment cells.

The posterior portion of the intestine is called the pars-nuda intestini or the ileum. It runs from the 13th to the 18th segments, where it passes into the hind gut. It is rather a wide and thin-walled tube with uniform cylindrical epithelium (Fig. XVIII). White waste matter is present in it. In a transverse section it shows that it consists of an epithelial layer covered by membrana propria which itself is surrounded by circular and longitudinal muscle fibres. It is surrounded by pads of muscles which help to press out the waste matter.

(*c*) *Stomach gland*:—On removing the carapace of the cephalothorax this gland with a median anterior and two lateral lobes is seen (Fig. XIV, 3). It was taken by Huxley and others as the salivery gland but Blanchard has stated that the scorpions possess no salivary gland and hence the above name has been adopted (Pavlovsky). It occupies the cephalothoracic cavity and posteriorly it is bounded by the diaphragm. The gland consists of numerous vesicles of glandular epithelium (Fig. XX). The cells very much resemble those of hepatopancreas but they differ from the latter by their narrower form. In section the epithelium appears to rest on the basal membrane which is surrounded by a peritoneal lining filling up the slits between the lobules of the gland.

(*d*) The hepatopancreas is a large brownish gland occupying the whole of the preabdomen (Fig. XIV, 4). It has a dorsal median depression in which lies the heart enclosed in the pericardial sac. The other internal organs in the preabdomen are embedded in the liver. It is a lobulated structure with its lobules being present only on its outer surfaces. It has on each side six vertical openings for the passage of the dorsoventral muscles which bound the sternites to the tergites.

As already mentioned the midgut receives from each side five ducts of the liver. These ducts branch repeatedly in the substance of the gland and ultimately end in the cavities in its lobules. Thus the ramiferous liver has a cavity which is continuous with that of the midgut. The liver of the scorpion is constructed after that of Crustacean Decapoda, as in *Cancer* Pearson has shown that it gives off the ducts on both sides which end in the cavities of the liver lobules. Both have got a similar cell structure.

In microtome sections of its lobules it appears to consist of the epithelium, the membrana basilaris and the peritoneal covering. The epithelial cells are of two kinds (Fig. XXII). The resorption cells (6) forming one of these kinds, are large and their nuclei are situated in the middle or near the base of the cell. There are globules of different sizes in the cell. The cell has a definite outline on the basal side. Its protoplasm has pigment granules which, are of excretory function. These cells also absorb the food particles.

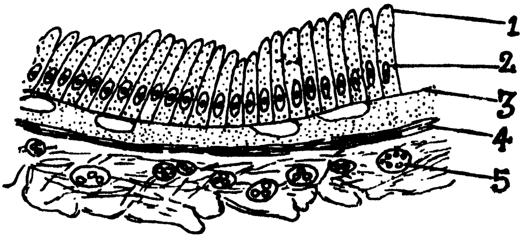


FIG. XVIII. T. S. of a portion of pars nuda intestini.
1 Epithelium, 2 Nucleus, 3 Membrana propria,
4 Circular muscles, 5 Longitudinal muscles.

The other type includes the ferment cells (7) which are rather fewer compared with the absorbing ones. They stain deeply with hematoxylin. The protoplasm of these cells contains numerous granules, filaments, etc. The cells are compressed and lie close to each other. The ducts of the liver have the same structure as the liver lobules.

THE HINDGUT OR PROCTODAEUM

The hind gut is an extremely short portion of the alimentary canal, which occupies the region of the last post-abdominal segment (Fig. XIV). Its inner wall is lined by chitin which is continuous with the chitin of the soft articulation membrane between the telson and the last segment. Outside the chitin of the hind gut there is an epithelial layer. The gut opens on the ventral side by the anal aperture which is surrounded by four protuberances (Fig. XIX). There are four hard chitinous platelets attached to these protuberances. When the posterior portion of the intestine is contracted the anal aperture becomes closed by these platelets. These platelets work simultaneously. The posterior portion of the hind gut is connected by oblique muscles to the middle of the last segment. This muscle is called m. levator ani (Fig. XIV).

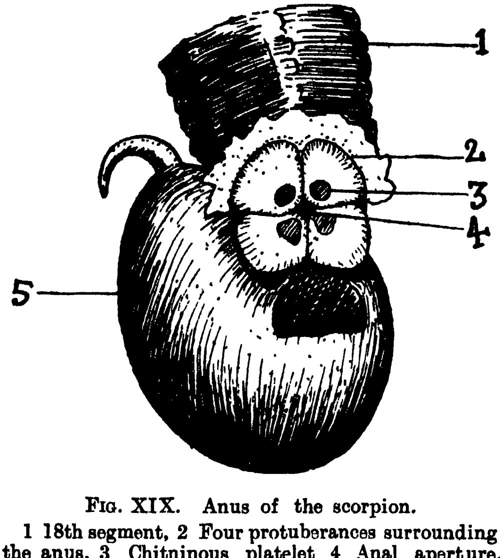


FIG. XIX. Anus of the scorpion.
1 18th segment, 2 Four protuberances surrounding the anus, 3 Chitninous platelet 4 Anal aperture, 5 Telson.

CIRCULATORY SYSTEM

The circulatory system is very well developed and consists of the heart, the arteries and the veins. The animal has a far more definite system of blood-vessels than any other Arthropod.

Heart :—On removing the terga of the preabdomen, the heart of the scorpion is seen situated beneath the muscles of the segments along the dorsal median ridge of the liver (Fig. XXII). It extends from the diaphragm (6th segment) to the last segment of the preabdomen (13th segment). It is an elongated and strongly muscular organ and lies in a thin-walled sac the pericardial sinus. The heart is suspended in the pericardial space by two sets of bands in each segment. These bands called the alæ cordi are of fibrous connective tissue stretching from the angles of heart to the wall of the pericardium. The heart leads anteriorly

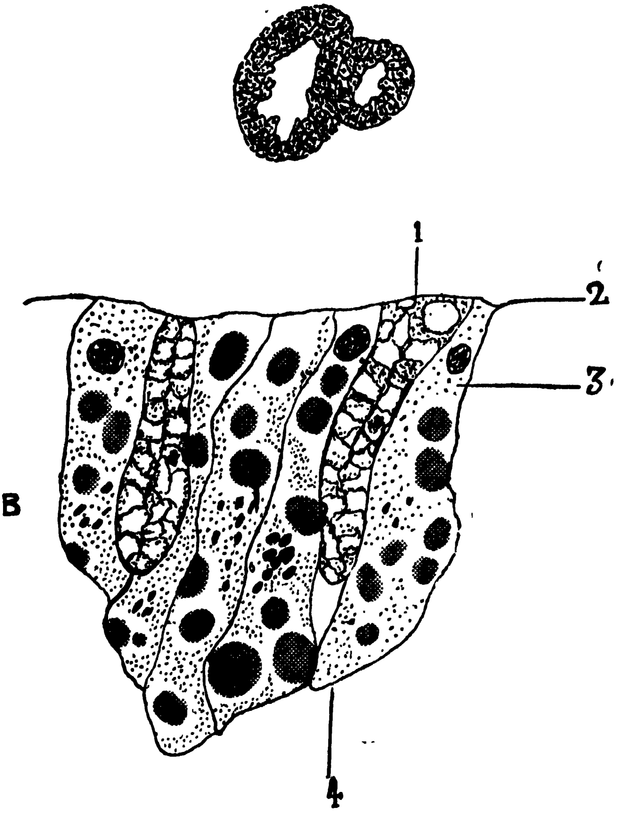


Fig. XX. T. S. of the stomach gland.

A. A complete section of the stomach gland. ×80

B. A portion of the wall of the stomach gland. ×900.

1 Ferment cells, 2 Membrana propria, 3 Resorption cell, 4 Free surface of the epithelial.

into a short trunk called the anterior aorta and posteriorly ends into the posterior artery. It is segmentally divided into seven different chambers each of which opens into the pericardial sinus by a pair of auricular openings called the ostia. These ostia are situated on the dorsolateral surface of each chamber, and are provided with valves which prevent the blood from re-entering the pericardium from the heart, so that it is forced to pass out of the heart by the arteries which start from it. The heart is clothed from outside by connective tissue layers which are connected with the alæ cordis In the wall of the heart are inserted semicircular transversely striated muscle fibres (Fig. XXIII) exterior to which fare found fine longitudinal ones.

Each chamber of the heart is pear-shaped in structure and gives off a pair of systemic arteries, from the ventral side for the supply of the viscera (Fig. XXII). It has two sets of alæ cordis attached to its corners (Fig. XXIII). The anterior set of muscles is longer and assists to dilate the chamber and to draw it forwards in the segment, while its contraction is brought out by the muscles of its wall. The second set or the posterior alæ cordis, which are retractor muscles of the chamber, originates from the posterior lateral part of the chamber and is directed backwards and outwards, and thus a gap is left between the two sets of muscles for the passage of the systemic vessels. The posterior set seems to be the first to act in dilating the chamber.

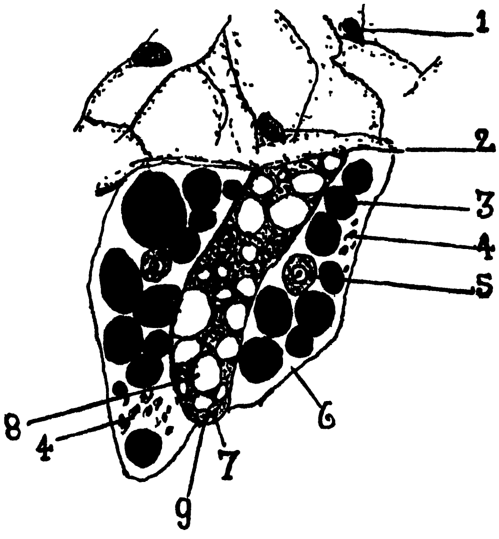


FIG. XXI. T. S. portion of hepatic lobule. ×900.

1 Peritoneal covering the of liver, 2 Membrana propria, 3 Acidophile inclusions of re-sorption cells, 4 Pigment inclusions, 5 Nucleus, 6 Resorption cell, 7 Ferment cells, Granular globular inclusions of ferment cells, 9 Basophile granules in protoplasm.

Out of the seven chambers of the heart the sixth is the largest, the seventh is rather small, while the remaining ones become gradually reduced in size from the fifth to the first chamber.

The valve of each ostium is formed by the duplication of the muscular layer on the dorsal surface of the heart. Thus the rows of circular fibres take part in the formation of the valve. As already mentioned, the systemic arteries (Fig. XXIII) are given off from the ventral side of the heart. From the anterior end of the heart a median arterial trunk known as the anterior aorta and two small lateral arteries are given off (Fig. XXII). These two lateral arteries give off many branches to supply the diaphragm and the posterior portion of the thorax.

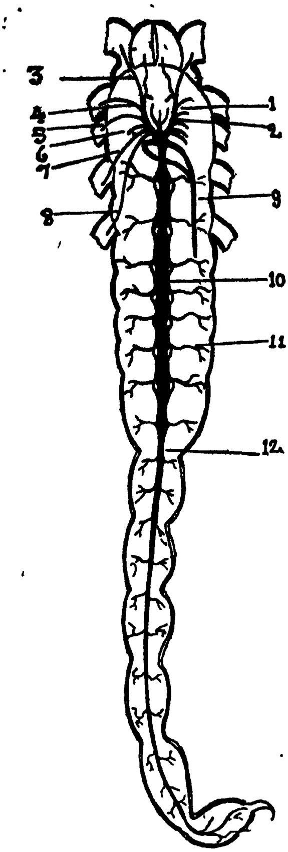


FIG. XXII. Circulatory system (diagrammatic.)
1 Lateral artery, 2 Cephalic artery, 3 Artery to the pedipalp, 4, 5, 7, and 8 Arteries of the legs, 6 Artery of the thorax, 9 Supraspinal artery, 10 Heart, 11 Systemic artery 12 Posterior artery.

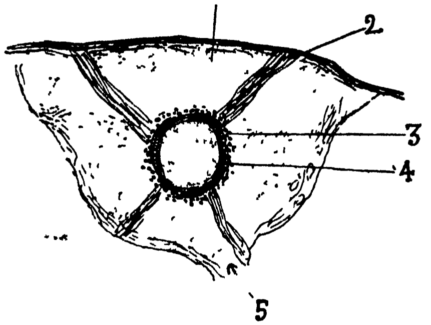


FIG. XXIII. T. S. of the heart, the pericardial sinus and the ali cardi muscle.
1 Pericardial sinus, 2 Alæ cordis muscle, 3 Longitudinal muscle layer, of the heart, 4 Circular muscle of the heart, 5 Opening of the veno-pericardiac vein .

Anterior aorta :—The anterior aorta starts from near the diaphragm and descends anteriorly. It is short and thick and proceeds obliquely forwards and downwards and passes beyond the central arch of the endosternite. Here it is slightly dilated and runs along the dorsal side of the œsophagus. Just at the point of its dilatation it gives off a pair of arteries towards the ventral side (Fig. XXII), which run around the œsophagus forming a vascular collar and unite with each other to form the supraspinal artery. This artery runs backwards along the nerve cord. As the aorta runs along the œsophagus, at a short distance behind the brain it gives off the second pair of arteries which supply the 4th pair of legs. Next the third pair of arteries is given off to supply the 3rd pair of legs. Just near the third pair of arteries a smaller fourth pair is given off which is distributed to the thorax. After giving off these branches the main aorta widens and then divides into three more branches of which the middle one forms the cephalic artery, while the two laterals run along the sides of the brain (Fig. XXIV). As these lateral vessels pass anteriorly

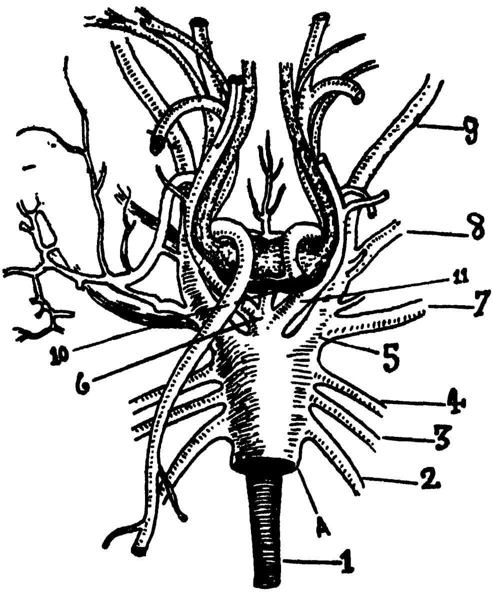


FIG. XXIV. Distribution of the cephalic blood vessels.

1 Supra-spinal artery, 2 Thoracic artery, 3, 4, 7, & 8 Arteries of the legs, 5 Lateral artery, 6 Cephalic artery, 11 Lateral branch of the cephalic artery, 10 Cerebral artery, 9 Artery to the chelicera.

they give off branches to the first and second pairs of legs and then pass into the pedipalps. Before going to the pedipalps each of the lateral trunks gives off a branch which turns up towards the dorsal side to unite with its fellow of the other side and with the branches of the cerebral artery. This branch of the lateral vessel supplies the muscles on the dorsal side of the brain and the stomach gland.

The short and median cephalic artery divides into three branches just after its origin. The median branch which may be called the *cerebral artery* gives out small branches to the brain and then it passes along and beyond dorsal brain and supplies the parts of the anterior thorax and the pharynx. It also gives branches which anastomose with the branches of the lateral arteries of the aorta as already mentioned. Thus a complete arterial network is formed around the brain. The two lateral branches of the cephalic artery run along the sides of the brain ; each one gives a big branch which runs along the great median optic nerve and divides into minute ramifications to supply the median eyes and the carapace. Just near this great branch of the cephalic lateral artery, a small branch is given off to supply the lateral eyes. This small branch also runs along the nerve which supplies the lateral eyes. Then the lateral cerebral artery begins to turn inwards towards the middle and gives off a small branch which runs backwards and outwards in the muscles of the thorax. According to Newport,[6] this branch forms two anastomoses with branches from the great sub-œsophageal division of the artery. The lateral cephalic artery then runs along the inner side of the strong muscles of the chelicerae where it divides into two branches ; the bigger one supplying the muscles of the chelicerae, and the smaller one going to the chelicerae where it is again divided into two to supply the movable and immovable fingers of the chelicerae.

Abdominal arteries :—The anterior aorta gives off ventrally a pair of small arteries, at its beginning the visceral arteries, supplying the intestine and the hepatopancreas. They run along the sides of the intestine and give branches to the heptopancreatic lobules along its ducts. They make extensive anastomoses along the length of the alimentary canal with branches from the systematic arteries.

The supraspinal artery formed by the union of the 1st anterior branches of the anterior aorta runs along the whole length of the nerve-cord giving off from its ventral surface single short branches at the anterior and posterior ends of each ganglion. At each of the posterior and anterior ends of the terminal ganglion of the nerve cord it gives off a pair of lateral arteries between the usual single anterior and posterior ganglionic arteries. These arteries supply the muscles and structure of that segment. The supra-spinal artery then passes on for a short distance between the pair of terminal nerves and then it divides into two branches to run along them. Each of these terminal arteries gives off a branch which sub-divides into anterior and posterior branches supplying the intestine. The terminal arteries themselves run along the terminal nerves and its branches and sub-branches run along the nerves to their ultimate distribution. Their branching takes place always immediately anterior to that of the nerves.

Posterior artery :—The seventh chamber of the heart is very small and seems to direct the current of the blood backwards into the posterior or caudal artery. The systemic arteries given off from this chamber show a deviation in their course : they are directed backwards instead of passing laterally forwards. The caudal artery passes posteriorly along the dorsal side of the intestine and at the posterior end of the 13th segment (7th abdominal segment) gives off a vessel on its ventral side which divides into three branches. The two lateral branches pass backwards along the hindmost lobe of the heptopancreas, and pass into the thick muscles of the 14th segment (1st post-abdominal segment) while the remaining or median vessel passes backwards below the caudal artery and is united with the supra-spinal artery.

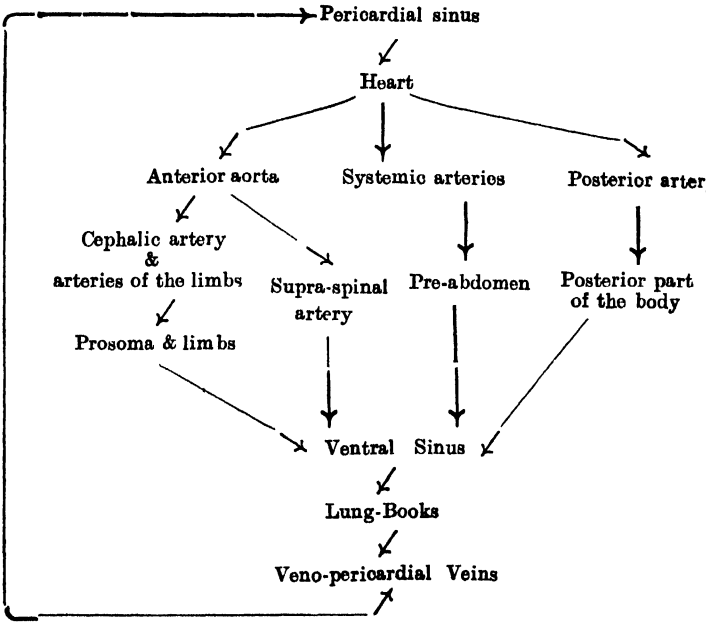
In the first post-abdominal segment the caudal artery gives off four pairs of vessels. According to Newport the first two pairs are directed laterally forwards, the third pair backwards and all these supplying the great flexor muscles in the dorsolateral regions of the segment. The fourth pair passing round the intestine unites with the supraspinal vessel. At the anterior as well as the posterior end of each postabdominal segment a pair of vessels are given off which supply the strong muslces of the post abdomen.

The venous system :—The blood is recollected by capillaries into the ventral sinus. The venous system consists of two main sinuses : (*i*) the pericardial sinus and (*ii*) the ventral sinus. The wall of the pericardium is fibrous and complete and when the heart is contracted it holds a considerable quantity of blood. When the heart expands this blood rushes into it through the ostia. There are seven pairs of veins, one pair in each segment (7 to 13 segments); which bring the blood from the lung books and open into the pericardium. These veins run ventro-dorsally along the veno-pericardial muscles.

The ventral sinus is situated on the ventral side in a median position. It has a small lateral expansion round each lung book. The dorsal wall of the ventral sinus and the floor of the pericardium are connected by seven pairs of vertical muscle bands, a pair in each segment of the mesosona. These veno-pericardial muscles were figured by Newport but not described, and later on, Lankester first recognised their importance. The venous blood from the body is brought to the ventral sinus by small vessels. From there it then goes through the lateral expansions to the lung books, where it is oxygenated. When the veno-pericardial muscles contract the pericardial sinus increases in volume and the blood from the lung books goes to the pericardial sinus from where it passes by the ostia into the heart.

The Blood:—The blood is more or less colourless with a slight bluish tinge, owing to the presence of certain dissolved pigments. Its liquid medium is known as the plasma and it contains a number of small amœbaid nucleated colourless carpuscles called amœbocytes.

The course of the blood may diagrammatically be represented a follows:—



(*To be continued*)

A NEW SPECIES OF AVIAN CESTODE FROM INDIA

By

N. B. Inamdar, M.Sc.,

Biology Department, Karnatak College, Dharwar

WHILE engaged in examining a collection* of Helminthes made during the last few years I came across four specimens of a Cestode belonging to the genus Shipleyia Fuhrmann 1908, from the intestine of a Black-winged Stilt, *Himantopus himantopus* (Linnæus). This genus was created by Fuhrmann to include a Cestode obtained by him from *Grathnago gigantea* from Vienna. So far the genus contains only one species *Shipleyia inermis* Fuhrman 1908. The species described in this paper is another.

SHIPLEYIA FARRANI SP. NOV.

Anatomy :—The maximum length of a full grown specimen is about 120 to 130 mm. and the maximum width is 5 mm. All the segments are broader than long. Mature proglottis measures 0.1 mm. in length and 0.33 mm. in maximum width.

The scolex (fig. 1) is 0. 4 mm. in diameter. The rostellum is absent Instead of the rostellum there is a papilla in the same position measuring 0.16 mm. in length. Suckers are nearly globular measuring 0.14 mm. in diameter and without hooks. The genital pores are irregularly alternating and are situated near the lateral margin of the proglottis. In this respect the arrangement varies from that of *Shipleyia inermis* Fuhrmann 1908.

The testes (fig. 2, T) are present only in a few mature segments and are about eight in number, situated anteriorly to ovary, each measuring about 12 μ in diameter.

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* I am thankful to the University of Bombay for the Research Grant given to me for this work to be carried out at the Karnatak College, Dharwar.

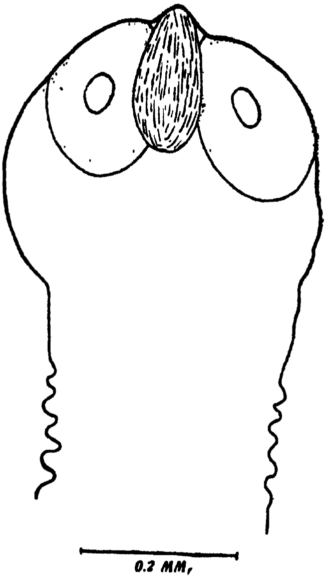

Fig. 1

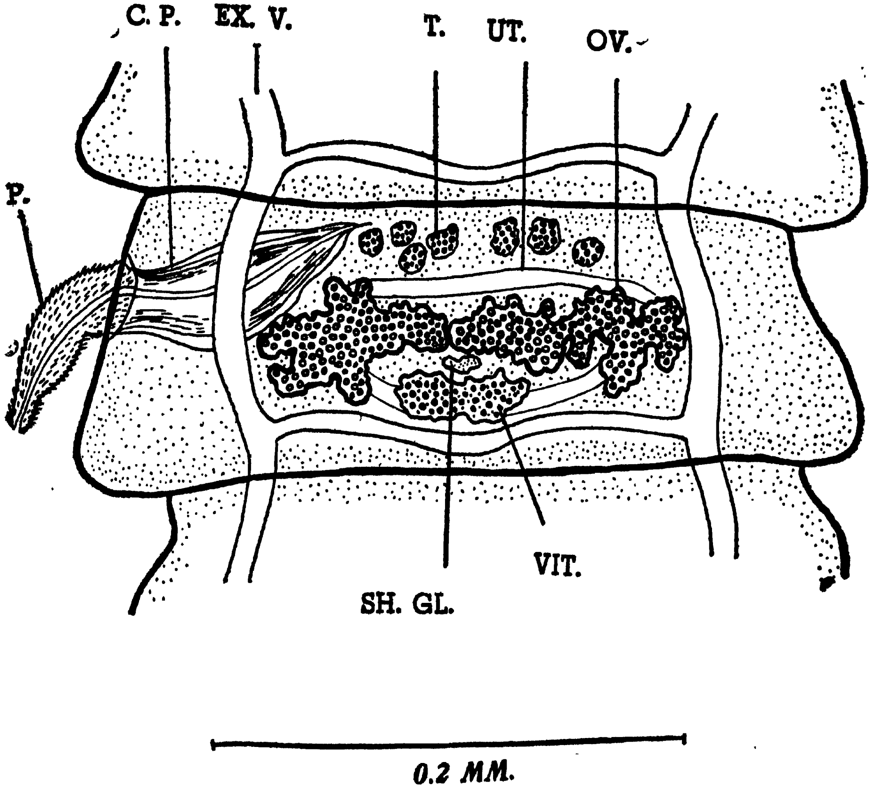

Fig. 2

Vas deferens is not visible. The cirrus sac (C. P.) is elongated and varies in diameter measuring 0.45 mm. in length and extends beyond the lateral excretory vessels. It contains a well-developed cirrus (P) which in many segments is extended. In fully extended condition (fig. 3) it measures 0.33 mm. in length and 0.1 mm. in maximum width. In shape it resembles a narrow high cone and is very powerfully armed with backwardly directed hooks. As observed by Furhmann the arrangement of hooks resembles very much that of the Acanthocephala. The size of hooks varies at different regions, being largest at the base. The cirrus sac opens into a lateral genital atrium.

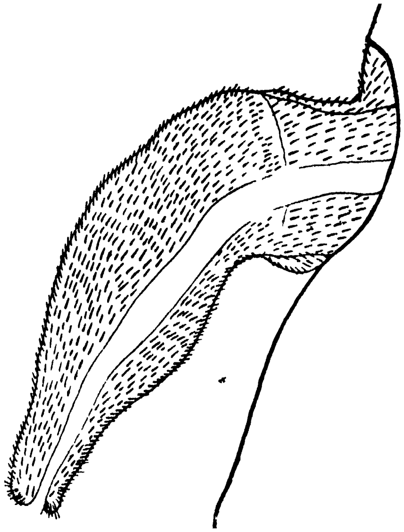

Fig. 3

The ovary (OV) is bilobed, situated in between two lateral excretory vessels. The vitelline gland (VIT) is situated posterior to the ovary. A small shell gland (SH. GL) is also visible in between the two lobes of the ovary. The female genital duct is absent.

The uterus (UT) in the mature segment is ring-shaped. Later on it becomes sacculated (fig. 4) all the sacs being more or less in lengthwise direction.

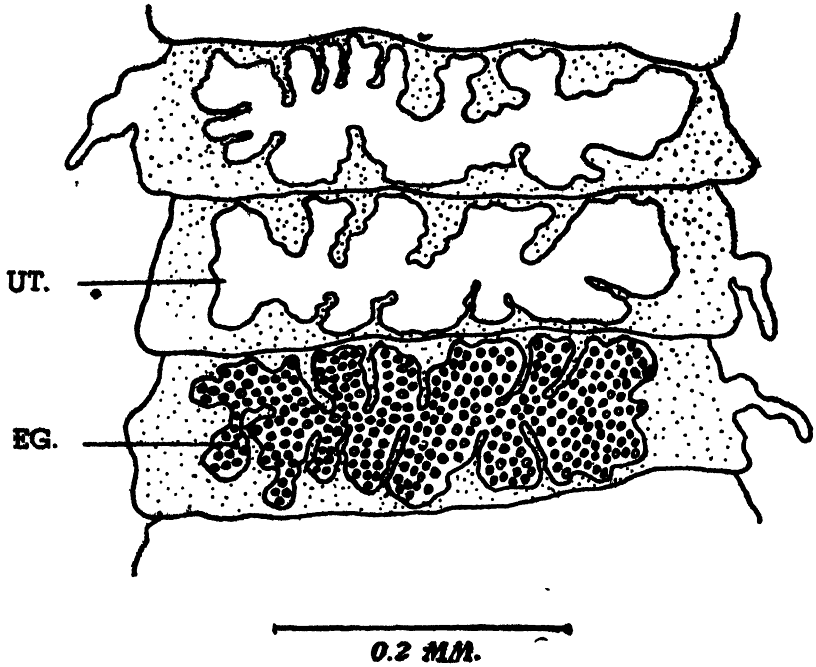

Fig. 4

The muscles are very powerfully developed. There are (fig. 5) three rows of transverse muscle layers, and in between them two rows of longitudinal muscle layers arranged in bundles. In addition to this, muscle fibres are running in different directions. It is also found that the cirrus sac runs ventrally to the ventral longitudinal excretory vessel.

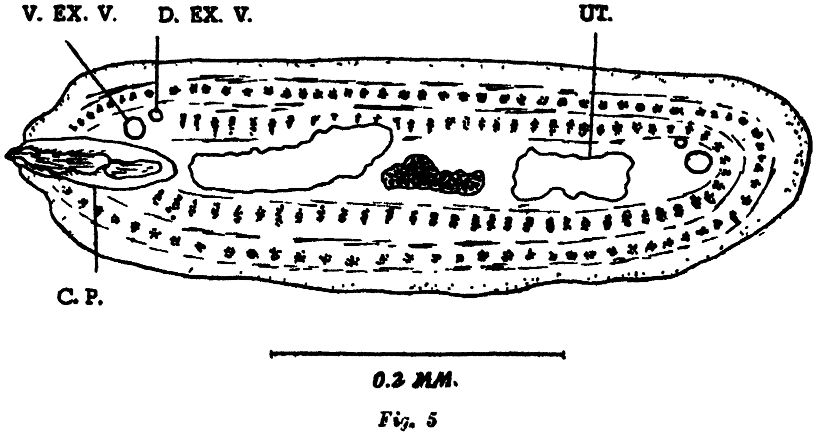

Fig. 5

DISCUSSION

The worm belongs to the family Acœleidæ in virtue of its characteristic musculature, cirrus and the absence of vagina. The characteristics of this worm namely absence of buds, monœcious strobilus, numerous proglottids with male glands anterior to female glands, one genital pore in each proglottid, unarmed scolex, and armed cirrus, place this worm in the genus *Shipleyia* Fuhrmann 1908. The species can be distinguished from *Shipleyia inermis* Fuhrmann 1908 by the difference in the arrangement of genital pores which is the most striking difference. In the genus Shipleyia as defined by Fuhrmann the male genital pores are regularly alternating. This definition needs to be emended in the light of the preceding observation. The male genital pores may be regularly or irregularly alternating. In addition to this the difference in size of the scolex, suckers and other structures is also very striking. I consider it, therefore, to be a new species for which I propose the name *Shipleyia farrani* after Principal A.C. Farran of this College to whom I am greatly indebted. The following is the specific diagnosis :—

Length 120 to 130 mm., maximum width 5 mm. ;
Diameter of Scolex 0.4 mm., unarmed, rostellum absent ;
A papilla present ;
Suckers four, each 0.14 mm., devoid of hooks ;
Testes about 7 to 8, anterior to ovary, each 12 μ in diameter ;
Cirrus pouch long, measuring 0.33 mm. × 0.1 mm. ;
Ovary bilobed ;
Vagina absent ;
Host—Himantopus himantopus (Linnæus) ;
Habitat—Intestine ;
Locality—Dharwar, Bombay Presidency, India.

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Name of the Candidate	Title of the Theses	Teacher	Place of Research	Remarks
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Ghatage, V. M. ..	A leaf spot disease of Dodonaea-viscosa L. caused by *Cersospora mitteriana* Syd.	Professor S. L. Ajrekar ..	F. C.	
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Phadnis, B. A. ..	Floral organogeny, structure and development of the micro—and megaspores and their gametophytes in Kigelia ponnata DC.	Professor S. V. Shevade ..	B. C.	
Shirke, V. S. ..	A study of the important katabolic changes in seedlings of *Avicennia officinalis* Binn.	Dr. F. R. Bharucha	R. I. Sc.	
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Mulkerkar, L. G. (Miss) ..	Studies on Comparative Anatomy of Cyprinids of Bombay	Professor P. R. Awati	R. I. Sc.	

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- Division of Plant Industry, 590, Vermeulen Street, Pretoria, Transvaal.
- *Faculty of Science, Imperial University of Osaka, Osaka, Japan.
- Field Museum of Natural History, Roosevelt Road and Lake Michigan, Chicago.
- Imperial Bureau of Plant Genetics, School of Agriculture, Cambridge, England.
- Indian Research Institute, 170, Maniktola Street, Calcutta.
- John Hopkins University, Baltimore, Maryland.
- †Kamarupa Anusandhan Samiti, Assam Research Society, Gauhati (Assam).
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A NOTE ON A DEFINITE INTEGRAL

By

THE LATE PROF. J. C. SWAMINARAYAN*

TO evaluate $u = \int_0^\infty \frac{\tan^{-1} a^2t^2}{1+t^2}\, dt$

This is a convergent integral and a^2 is put in as a square as it must be the intention to consider only positive values of the parameter.

$$\frac{\partial u}{\partial a} = \int_0^\infty \frac{2at^2}{(1+a^4t^4)\,(1+t^2)}\, dt$$

$$= \frac{2a}{1+a^4} \int_0^\infty \left\{ \frac{1+a^4t^2}{1+a^4t^4} - \frac{1}{1+t^2} \right\} dt$$

by partial fractions.

Now use the result

$$\int_0^\infty \frac{x^{2m}\, dx}{1+x^{2n}} = \frac{\pi}{2n} \frac{1}{\operatorname{Sin}\frac{2m+1}{2n}\pi}$$

and we get

$$\frac{\partial u}{\partial a} = \frac{2a}{1+a^4} \left[\frac{\pi}{2\sqrt{2}\,a} + \frac{a\pi}{2\sqrt{2}} - \frac{\pi}{2} \right]$$

$$= \frac{\pi}{\sqrt{2}} \frac{1}{1+a^4} \left(1 - a\sqrt{2} + a^2 \right)$$

$$= \frac{\pi}{(a^2+a\sqrt{2}+1)\sqrt{2}}$$

$$= \frac{\pi/\sqrt{2}}{(a+1/\sqrt{2})^2 + (1/\sqrt{2})^2}$$

---

*The note is from a letter which the late Professor Swaminarayan sent to me on January 10, 1942.—G. S. Mahajani.

$$\therefore u = \frac{\pi}{\sqrt{2}} \sqrt{2} \tan^{-1}(\alpha\sqrt{2}+1) + c$$

Now u and α vanish together and hence $c = -\pi^2/4$

$$\therefore u = \pi\left[\tan^{-1}(\alpha\sqrt{2}+1) - \tan^{-1} 1\right]$$

$$= \pi \tan^{-1}\frac{\alpha\sqrt{2}}{2+\alpha\sqrt{2}}$$

$$= \pi \tan^{-1}\frac{\alpha}{\alpha+\sqrt{2}}$$

2. The particular case $\alpha=1$ is interesting and can be worked out independently :—

$$I = \int_0^\infty \frac{\tan^{-1} t^2}{1+t^2}\, dt$$

$$= \int_0^1 + \int_1^\infty = I_1 + I_2 \quad \text{, say.}$$

Now in $I_2 = \int_1^\infty \frac{\tan^{-1} t^2}{1+t^2}\, dt,$

put $t = \frac{1}{\xi}$ and we get

$$I_2 = \int_0^1 \frac{\tan^{-1}(1/\xi^2)}{1+1/\xi^2} \frac{d\xi}{\xi^2}$$

$$= \int_0^1 \frac{\pi/2 - \tan^{-1}\xi^2}{1+\xi^2}\, d\xi$$

$$= \frac{\pi}{2}\int_0^1 \frac{d\xi}{1+\xi^2} - I_1$$

$$\therefore I = I_1 + I_2 = \frac{\pi}{2}\int_0^1 \frac{d\xi}{1+\xi^2} = \frac{\pi^2}{8}$$

Thus $\int_0^\infty \frac{\tan^{-1} t^2}{1+t^2}\, dt = \frac{\pi^2}{8}$

INTERPOLATION AND SUMMATION FORMULAS AND THE PROPERTIES OF FACTORIALS—II

By

DR. D. K. SEN

10. *MEAN Value of $F_n(x)$ in the interval $(r, r+1)$, where r is an integer less than n.* Since $|F_n(x)| = |F_n(n-x)|$, we need consider only the first $\frac{1}{2}n$ intervals if n be even, and the first $\frac{1}{2}(n+1)$ intervals if n be odd. Let us use the symbol $M_{n,r}$ to denote this mean. Then

$$M_{n,r} = \frac{\int_r^{r+1} F_n(x)\,dx}{(r+1)-r} = \int_r^{r+1} F_n(x)\,dx$$

$$= \int_0^1 F_n(x+r)\,dx. \tag{18}$$

Now, the positive quantity

$$-\frac{F_n(x)}{F_n(x+1)} = \frac{n-x}{x+1} = \frac{n+1}{x+1} - 1\,;$$

therefore, this is a decreasing function of x when $x>0$; and in the interval $(r, r+1)$,

$$\frac{n-r-1}{r+2} < -\frac{F_n(x)}{F_n(x+1)} < \frac{n-r}{r+1}.$$

Hence we shall have

$$\frac{n-r-1}{r+2} < -\frac{M_{n,r}}{M_{n,r+1}} < \frac{n-r}{r+1}, \tag{19}$$

as well; put $r=0, 1, 2, \ldots r-1$ in succession and multiply the results together. We then get

$$\frac{(n-1)\,(n-2)\,\ldots\,(n-r)}{(r+1)\,!} < \frac{(-1)^r\,M_{n,\,0}}{M_{n,\,r}}.$$

$$< \frac{n\,(n-1)\;\ldots\;(n-r+1)}{r\,!}. \tag{20}$$

From (19) we see that $-\dfrac{M_{n,\,r}}{M_{n,\,r+1}} > 1$ if $r+2 \leqslant n-r-1$, or if, $r+1 \leqslant \frac{1}{2}(n-1)$; and that this quantity <1 if $r+1 \geqslant n-r$, or if, $r+1 \geqslant \frac{1}{2}(n+1)$. In other words, $M_{n,\,r}$ decreases in absolute value as one proceeds towards the centre of the range (o, n),—an expected result. Thus the greatest mean for a given value of n, is $M_{n\;0}$ and the least is $M_{n,\,\frac{1}{2}n}$ or $M_{n,\,\frac{1}{2}n-1}$ when n is even, and $M_{n,\,\frac{1}{2}(n-1)}$ when n is odd. And, the ratio of the greatest to the least mean lies between the limits given by (20).

For large values of n, Stirling's theorem shows that the upper limit approximates to $\dfrac{2^n}{\sqrt{\pi}}$, and the lower limit to $\dfrac{2^{n-1}}{\sqrt{\pi\, m^3}}$, where $m=\frac{1}{2}\,n$ when n is even, and $m=\frac{1}{2}\,(n-1)$ when n is odd.

Each of these values tend to infinity when $n \longrightarrow \infty$.

Like the maximum values of the ordinates, I have calculated the magnitudes of the means for $n=1, 2, \ldots 10$, and the results are arranged in the following Table.

TABLE III

n	No. of diff. means	Magnitudes of means	Ratios to the least	Successive ratios
1	One	$\frac{1}{6}$	....	....
2	One	$\frac{1}{4}$	....	....
3	Two	$\frac{19}{30}$; $\frac{11}{30}$	19 : 11	1.73
4	Two	$2\frac{1}{4}$; $\frac{11}{12}$	27 : 11	2.45
5	Three	$11\,\frac{23}{84}$; $3\frac{19}{84}$; $2\frac{23}{84}$	4.52: 1.42 : 1	3.18 1.42
6	Three	$57\frac{7}{24}$; $14\frac{5}{8}$; $7\frac{23}{24}$	7.20: 1.84 : 1	3.92 1.84

TABLE III—(*contd.*)

n	No. of diff. means	Magnitudes of means	Ratios to the least	Successive ratios
7	Four	$377\frac{23}{90}$; $81\frac{7}{90}$; $35\frac{83}{90}$; $27\frac{67}{90}$	13.60 : 2.92 : 1.29 : 1	4.60 2.26 1.29
8	Four	$2864\frac{1}{20}$; $531\frac{1}{4}$; $198\frac{9}{20}$; $124\frac{17}{20}$	22.94 : 4.26 : 1.59 : 1	5.39 2.68 1.59
9	Five	$24624\frac{65}{132}$; $4016\frac{1}{132}$; $1296\frac{65}{132}$; $688\frac{1}{132}$; $560\frac{65}{132}$	43.93 : 7.17 : 2.31 : 1.22:1	6.13 3.10 1.88 1.22
10	Five	$236469\frac{3}{8}$; $34400\frac{1}{24}$; $9776\frac{1}{24}$; $4495\frac{3}{8}$; $3082\frac{17}{24}$	76.73 : 11.16 : 3.17 : 1.46:1	6.88 3.52 2.17 1.46

If we denote by q_n the ratio of the greatest to the least magnitudes of the means of $F_n(x)$ in the various intervals $(r, r+1)$, we can get the following relations as in the case of p's.

$$\frac{2}{m+1} < \frac{q_{2m+1}}{q_{2m}} < \frac{2m+1}{m} \text{ or } 2+\frac{1}{m}. \tag{21}$$

$$\text{And, } \frac{2m+1}{m+2}, \text{ or } 2-\frac{3}{m+2} < \frac{q_{2m+2}}{q_{2m+1}} < \frac{2m+2}{m+1}, \text{ or } 2. \tag{22}$$

We thus observe that $\frac{q_{n+1}}{q_n} \longrightarrow 2$ when $n \longrightarrow \infty$.

§ 3. SOME DEFINITE INTEGRALS INVOLVING $F_n(x)$

11. Three definite integrals (*viz.*, L_p, K_{2p}, M_{2p}) were introduced by Gauss and Laplace in connection with the summation formulas associated with their names. A number of formulae in these integrals have been found by the above-named mathematicians and others. In this section I have given new formulae [*viz.*, (40), (42), (47), (51*a*), (51*b*), (52), (53), (56), (57), (64), (65), (67), (69), (71), (73), (75), (75*a*), (77) and (79)] as also new derivation of old ones [*viz.*, (48) and (66)]; and I have added a few other integrals (*viz.*, M'_{2p}, σ_{2p}, D_{2p+2}, σ'_{1p}) and discussed some of their properties.

The following integral

$$M_{2p} = \frac{1}{(2p)\,!}\int_{p-1}^{p} F_{2p-1}(x)\,dx$$

$$\frac{1}{(2p)\,!}\int_{0}^{1} F_{2p-1}(x+p-1)\,dx$$

$$= \frac{1}{(2p)\,!}\int_{-\frac{1}{2}}^{+\frac{1}{2}} x^{[2p+1]-1}\,dx \tag{23}$$

occurs in the second summation formula of Gauss (*cf.* Steffensen, *loc. cit.*, p. 109). From the above definition it appears that the integral $= \frac{\text{least mean of } F_{2p-1}(x)}{(2p)\,!}$. An integral of a similar type will be

$$M'_{2p} = \frac{\text{least mean of } F_{2p}(x)}{(2p+1)\,!} = \frac{1}{(2p+1)\,!}\int_{p}^{p+1} F_{2p}(x)\,dx$$

$$= \frac{M_{2p,\,p}}{(2p+1)!} = \frac{1}{(2p+1)!}\int_{0}^{1} F_{2p}(x+p)\,dx$$

$$= \frac{1}{(2p+1)!}\int_{0}^{1} x^{[2p+2]-1}dx\ . \tag{24}$$

As M'_{2p} is also equal to

$$-\frac{1}{(2p+1)\,!}\int_{p-1}^{p} F_{2p}(x)\,dx = -\frac{1}{(2p+1)\,!}\int F_{2p}(x+p-1)dx \tag{25}$$

we get

$$M'_{2p} = \frac{1}{2(2p+1)\,!}\int_{0}^{1}\Big\{F_{2p}(x+p) - F_{2p}(x+p-1)\Big\}\,dx \tag{26}$$

$$= \frac{1}{2(2p)\,!}\int_{0}^{1} F_{2p-1}(x+p-1)\,dx = \tfrac{1}{2}\,M_{2p}. \tag{27}$$

12. From definition, we have

$$(2p)\,!\ M_{2p} = \int_{0}^{1} F_{2p-1}(x+p-1)\,dx,$$

which by the repeated application of integration of parts,

$$= \Big[\,x\,F_{2p-1}(x+p-1) - \frac{x^2}{2\,!}F'_{2p-1}(x+p-1) + \frac{x^3}{3\,!}F''_{2p-1}(x+p-1) - \ldots + \frac{x^{2p+1}}{(2p+1)!}(2p)\,!\,\Big]_{0}^{1}, \tag{28}$$

$$= F_{2p-1}(p) - \frac{1}{2!} F'_{2p-1}(p) + \frac{1}{3!} F''_{2p-1}(p) - \ldots$$
$$\ldots + \frac{1}{2p+1}, \tag{29}$$

the number of terms in the series being $(2p+1)$. The first term is clearly zero. In order to evaluate the other terms we utilize the following result :

Let $f(x)$ be a product of n linear factors, that is,

$$f(x) = (x-a_1)(x-a_2)\ldots(x-a_n).$$

Then the *r-th* derivative of $f(x)$, or

$$f^r(x) = r! \times (\text{sum of products of the factors taken } n-r \text{ at a time}). \tag{30}$$

Now the factors of $F_{2p-1}(p)$ are o, p, and

$$\pm 1, \quad \pm 2, \quad \ldots \quad \ldots \quad \pm(p-1).$$

Let us introduce the symbol S^n_r to denote the sum of products taken r at a time, of the following squares of natural numbers :

$$1^2, 2^2, \ldots \quad \ldots \quad n^2 ;$$

and let S^n_{-r} denote the sum of products of the reciprocals of these squares, taken r at a time.

It is easy to see that

$$F'_{2p-1}(p) = (-1)^{p-1} (p-1)!\ p!,$$
$$F''_{2p-1}(p) = F'_{2p-1}(p)\ \frac{2!}{p},$$
$$F'''_{2ip-1}(p) = -F'_{2p-1}(p)\ 3!\ S^{p-1}_{-1},$$
$$F^{iv}_{2p-1}(p) = -F'_{2p-1}(p)\ \frac{4!}{p}\ S^{p-1}_{-1}, \text{ etc.} \tag{31}$$

Hence, we get

$$M_{2p} = \frac{(-1)^p (p-1)!\, p!}{(2p)!} \left\{ \tfrac{1}{2}\left(1 - \frac{2}{3p}\right) - \tfrac{1}{3}\left(1 - \frac{4}{5p}\right) S^{p-1}_{-1} \right.$$
$$\left. + \tfrac{1}{6}\left(1 - \frac{6}{7p}\right) S^{p-1}_{-1} - \ldots \text{ to } 2p \text{ terms} \right\} \ldots \tag{32}$$

When p is very large, the second terms in the small brackets can be neglected, and we have

$$M_{2p} \backsim \frac{(-1)^p \pi^{\frac{1}{2}}}{2^{2p+1}\, p^{\frac{1}{2}}} \left\{ 1 - \tfrac{1}{2} S_{-1} + \tfrac{1}{3} S_{-2} - \ldots \right\} \ldots \tag{33}$$

from Stirling's theorem, S_{-r} standing for S^n_{-n} when n is infinite. Now from a well-known trigonometrical result,

$$\frac{\sin \pi\sqrt{x}}{\pi\sqrt{x}} = \left(1 - \frac{x}{1^2}\right)\left(1 - \frac{x}{2^2}\right)\left(1 - \frac{x}{3^2}\right) \ldots\ldots, \tag{34}$$

it follows that

$$S_{-r} = \frac{\pi^{2r}}{(2r+1)}. \tag{35}$$

If we substitute these values in (33) we get the series in brackets

$$= \frac{2}{\pi^2}(1-\cos\pi) = \frac{4}{\pi^2}. \tag{36}$$

Therefore,

$$M_{2p} \backsim \frac{(-1)^p}{2^{2p-1}\pi^{3/2}p^{\frac{1}{2}}}. \tag{37}$$

For another method of derivation of this result see Steffensen, *loc. cit.*, p. 110.

13. *Recurrence formulæ for M's.*

(*i*) Let us assume

$$x^{2p} = a_{p,o}\, x^{[2p+1]-1} + \frac{a_{p,1}}{2^2} x^{[2p-1]-1} + \frac{a_{p,2}}{2^4} x^{[2p-3]-1} + \dots$$
$$+ \frac{a_{p,p-1}}{2^{2p-2}} x^{[3]-1} + \frac{a_{p,p}}{2^{2p}}. \tag{38}$$

These coefficients are different from the central differences of nothing. The a's can be found by expanding $x^{[n]-1}$ in power series and then equating coefficients of different powers of x; alternately, put $x = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ in succession. In each case we shall get a system of linear equations from which the values of the constants can be determined.

It is however easy to see that $a_{p,o} = 1 = a_{p\,p}$; $a_{p,1} = \frac{1}{3}p\,(4p^2-1)$; $a_{p,p-1} = \frac{1}{8}(3^{2p}-1)$.

It is possible to express the a's in terms of central differences. Put $f(x)$ for x^{2p}, and operate both sides of (38) by $\delta^2, \delta^4, \delta^6, \dots$, and put $x = \frac{1}{2}$ in each result. We shall then immediately obtain the following expressions for the coefficients :

$$\frac{a_{p,p-1}}{2^{2p-2}} = \frac{1}{2!}\delta^2 f(\tfrac{1}{2}),\quad \frac{a_{p,p-2}}{2^{2p-4}} = \frac{1}{4!}\delta^4 f(\tfrac{1}{2}),\ \text{etc.} \quad (39\cdot$$

The sets of coefficients will be different for different values of p; the easier and more practical way for determining the coefficients for the first few values of p at least, is by the method of synthetic division. If we put $2x = X$ and multiply (38) by 2^{2p}, we get

$$X^{2p} = a_{p,p} + a_{p,p-1}(X^2-1^2) + a_{p,p-2}(X^2-1^2)(X^2-3^2) + \cdot$$
$$\dots + a_{p,o}(X^2-1^2)\,X^2(-3^2)\dots\{X^2-(2p-1)^2\},$$

writing the terms in reverse order. The following scheme of synthetic division is now self-explanatory.

1^2)	1	0	0	0	0	0	0
3^2)	1	1	1	1	1	1	1
5^2)	1	10	91	820	7381	66430	...
7^2)	1	33	966	24970	631631	...	
9^2)	1	84	5082	274088	...		
11^2)	1	165	18447	...			
	1	286	...				

For any value of p, start with the 1 below the p-th zero (counting towards the right) in the first row, and proceed diagonally downwards and backwards; the figures will give the values of $a_{p,p}$, $a_{p,p-1}$, $a_{p,p-2}$ . . . in succession. For instance, for $p=4$, the corresponding figures are 1, 820, 966, 84, 1.

We shall suppose that the a's have been determined. We integrate both sides of (38) between the limits $-\frac{1}{2}$ and $+\frac{1}{2}$. Dividing the result by $(2p)$! we get the formula :

$$-\frac{p}{2^{2p-1}(2p+1)!} = M_{2p} + \frac{a_{p,1}}{2^2.2p(2p-1)} M_{2p-2} + \frac{a_{p,2}}{2^4.2p(2p-1)(2p-2)(2p-3)} M_{2p-4} + \dots \text{ to } p \text{ terms.} \qquad (40)$$

(*ii*) Let us next use the central differences of nothing and put

$$x^{2p+2} = c_{p,0}\,x^{[2p+2]} + c_{p,1}\,x^{[2p]} + c_{p,2}\,x^{[2p-2]} + \dots\dots + c_{p,p}\,x^{[2]}, \qquad (41)$$

where $c_{p,r} = \Delta^{2(p+1-r)}0^{2p+2}/(2p+2-2r)!$

The scheme for synthetic division for the first few c's are given below:

1^2)	1	0	0	0	0	0	0
2^2)	1	1	1	1	1	1	1
3^2)	1	5	21	85	341	1365	...
4^2)	1	14	147	1408	13013	..	
5^2)	1	30	627	11340	..		
6^2)	1	55	2002	..			
		91					

We have

$$M_{2p} = 2\,M' = \frac{2}{(2p+1)\,!}\int_0^1 x^{[2p+2-1}\,dx.$$

Therefore, if we divide (41) by x and integrate both sides between the limits 0 and 1, we shall get after a little simplification

$$-\frac{2p}{(2p+2)!} = M_{2p} + \frac{c_{p,1}}{(2p+1)\,2p}M_{2p-2}$$

$$+\frac{c_{p,2}}{(2p+1)\;2p\;(2p-1)\;(2p-2)}M_{2p-4} + \ldots \text{to } p \text{ terms.} \qquad (42)$$

(*iii*) Bessel's formula for interpolation with the remainder term is (*cf.* Steffensen, *loc. cit.*, p. 30) :—

$$f\,(x+\tfrac{1}{2}) = \sum_{n=0}^{p-1}\left[\frac{x^{[2n+1]-1}}{(2n)!}\,\Box\,\delta^{2n}\;f(\tfrac{1}{2}) + \frac{x^{[2n+1]}}{(2n+1)!}\,\delta^{2n+1}\,f(\tfrac{1}{2})\right]$$

$$+\frac{x^{[2p+1]-1}}{(2p)!}\;f^{\,2p}\,(\xi). \qquad (43)$$

Let us apply the formula to $f\,(x) = \cos\,(2x-1)\;\theta$, where θ is a constant that can be chosen conveniently. Then

$$\tfrac{1}{2}\,[\,f\,(x)\; + f\,(x+1)\,] = \cos 2x\,\theta.\;\;\cos\theta,\;\;\text{and}$$

$$\Box\;\delta^{2n}f\,(\tfrac{1}{2}) = 2\cos\theta\;[\,\cos 2n\,\theta - {}^{2n}C_1\cos 2\,(n-1)\,\theta$$

$$+\;{}^{2n}C_2\cos 2\,(\,n-2)\,\theta - \ldots]$$

$$= \cos\theta.\;\;2^{2n}.\;\;(-1)^n\;\;\sin^{2n}\theta, \qquad (44)$$

from a known trigonometrical result.

Integrate both sides of (43) between the limits $-\frac{1}{2}$ and $+\frac{1}{2}$ for the above assumed function and substitute the values from (44). We get

$$\frac{\sin\theta}{\theta} = \cos\theta + \sum_{n=1}^{p-1}\;(-1)^n\;M_{2n}\;\cos\theta.\;(2\,\sin\,\theta)^{2n} + R', \qquad (45)$$

where

$$R' = \int^{+\frac{1}{2}} \frac{x^{[2p+1]-1}}{(2p)!}\;f^{\,2p}\,(\xi)\;dx$$

$$= \quad M_{2p}.\,f^{\,2p}\,(\xi), \qquad (46)$$

by the Mean Value Theorem, since $x^{[2p+1]-1}$ has the same sign throughout the interval; the two ξ's are, of course, different.

Now,

$$f^{2}\;\;(x) = (-1)^2.\;\;(2\,\theta)^{2p}.\;\cos\;(2x-1)\;\theta.$$

Therefore,

$$|\,R'\,| \leqslant |\,M_{2p}.\,(2\theta)^{2p}\,| \leqslant \frac{(2p)\,!\,\theta^{2p}}{(p!)^{2}.\,2^{2p}}$$

$$=\theta^{2p}.\frac{2p-1}{2p}\quad\frac{2p-3}{2p-2}\cdots\cdots\frac{1}{2} < \theta^{2}\,,$$

since it has been proved in Steffensen's book, p. 110, that

$$|\,M_{2p}\,| \leqslant {}^{2p}C_p\,2^{-4p}.$$

So, $|\,R'\,| \longrightarrow 0$ when $p \longrightarrow \infty$, provided that $|\,\theta\,| < 1$. Hence we shall have

$$\frac{\tan\,\theta}{\theta} \text{ or } \frac{\sin\,\theta}{\theta\cos\,\theta} = 1+\sum_{n=1}^{\infty}\,(-1)^{n}\;M_{2n}\;(2\sin\,\theta\,)^{2n} \tag{47}$$

because $M_0=1$. The above result is proved for *any* value of θ, less than unity in magnitude. We note that M_2 is negative, M_4 positive, and so on alternately ; so that the infinite series (47) is really a series of positive terms. Applying D'Alembert's ratio test for convergency, we get

$$\frac{a_{n+1}}{a_n} = \left|\frac{M_{2n+2}}{M_{2n}}\right|.\;(2\sin\,\theta\,)^{2} \longrightarrow \sin^{2}\theta,$$

for large values of n, with the help of (37). Hence, the series will be convergent if $|\,\sin\theta\,| < 1$. It will, however, be divergent when $|\,\sin\theta\,| = 1$, as will be evident by comparing its terms with those of the divergent series $\Sigma\,\frac{1}{\sqrt{n}}$. This extends the range of convergency of the series to $0 \leqslant \theta < \frac{1}{2}\pi$. And as the left-hand side of (47) is the sum of this series for a *variable* θ although less than unity, the same must be the sum for the whole range of convergency.

If we put $\theta = \frac{\pi}{6}, \frac{\pi}{4}, \frac{\pi}{3}$ in succession in (47), we get the following interesting results :

$$\frac{\sqrt{3}}{\pi} = 1 + \sum_{n=1}^{\infty}\,\left|\,M_{2n}\,\right|,$$

$$\frac{4}{\pi} = 1 + \sum_{n=1}^{\infty}\,2^{n}\,\left|\,M_{2n}\,\right|, \text{ and}$$

$$\frac{3\sqrt{3}}{\pi} = 1 + \sum_{n=1}^{\infty}\,3^{n}\,\left|\,M_{2n}\,\right|.$$

(iv) We are now in a position to establish more recurrence formulæ for the M_{2p}'s. Multiply both sides of (47) by θ and expand in powers of $\sin\theta$, using the results

$$\theta = \sin\theta + \frac{1}{2}\frac{\sin^3\theta}{3} + \frac{1.3}{2.4}\frac{\sin^5\theta}{5} + \frac{1.3.5}{2.4.6}\frac{\sin^7\theta}{7} + \dots,$$

$$\tan\theta = \sin\theta + \frac{1}{2}\sin^3\theta + \frac{1.3}{2.4}\sin^5\theta + \frac{1.3.5}{2.4.6}\sin^7\theta + \dots$$

Equating coefficients of $\sin^{2p+1}\theta$ from both sides, we obtain after a little simplification, the formula

$$\frac{(-1)^p.\ 1.3\dots(2p-1)}{2^{2p}.\ 2.4\dots 2p}\left[1-\frac{1}{2p+1}\right]$$

$$= M_{2p} - \frac{1^2}{2^2.3!}M_{2p-2} + \frac{1^2.3^2}{2^4.5!}M_{2p-4} - \dots \text{ to } p \text{ terms,} \qquad (48)$$

which is the same as Steffensen's formula (cf. *Interpolation*, p. 191).

(v) Other recurrence formulæ, although with more complicated expression for the coefficients, can be derived from the formula (47). Let us, for example, expand both sides in terms of θ. We know that

$$\frac{\tan\theta}{\theta} = B_1\frac{2^2(2^2-1)}{2!} + B_3\frac{2^4(2^4-1)}{4!}\theta^2 + \dots, \qquad (49)$$

where the B's are the numbers of Bernoulli. Also,

$$\sin^{2n}\theta = \theta^{2n}\left(1 - \frac{\theta^2}{3!} + \frac{\theta^4}{5!} - \dots\right)^{2n}$$
$$= \theta^{2n}(b_{n,0} + b_{n,1}\theta^2 + b_{n,2}\theta^4 + \dots), \qquad (50)$$

suppose. We can find that

$$b_{n,0} = 1,\ b_{n,1} = -\frac{2n}{3!},\ b_{n,2} = \frac{2^2n(5n-1)}{3.5!},$$

$$b_{n,3} = -\frac{2^3n}{9.7!}(35n^2 - 21n + 4),$$

$$b_{n,4} = \frac{2n}{15.9!}(175n^3 - 210n^2 + 101n - 18),$$

etc. Substitute these in (47) and equate coefficients of θ from both sides. Then

$$(-1)^p B_{2p+1}\frac{4(2^{2p+2}-1)}{(2p+2)!} = M_2 - \frac{b_{,1}}{2^2}M_{2p-2} + \frac{b_{n,2}}{2^4}M_{2p-4}$$
$$+ \dots \text{ to } p \text{ terms.} \qquad (51a)$$

As another alternative let us expand both sides of (47) after multiplication by θ, in terms of powers of $\tan\theta$, it being understood that $|\theta| < \frac{\pi}{4}$ for this expansion. We get

$$\tan\theta = (\tan\theta - \tfrac{1}{3}\tan^3\theta + \tfrac{1}{5}\tan^5\theta - \dots)$$
$$+ \sum_{n=1}^{\infty} (-1)^n M_{2n} (2\tan\theta)^{2n}$$
$$\times \Big\{ (1 - n\tan^2\theta + \frac{n(n+1)}{2!}\tan^4\theta - \dots)(\tan\theta - \tfrac{1}{3}\tan^3\theta$$
$$+ \tfrac{1}{5}\tan^5\theta - \dots.) \Big\}.$$

Equate coefficients of $\tan^{2p+1}\theta$ from both sides; on division by $(-1)^p . 2^{2p}$, the result becomes

$$0 = \frac{1}{(2\quad +1)2^{2p}} + M_{2p} + \frac{3p+1}{13.2^2} M_{2p-2} + \frac{1}{30.2^4} M_{2p-4} (15p^2$$
$$+25p+6) + \frac{1}{210.2^6} (35p^3 + 35p^2 + 112p + 30) M_{2p-6}$$
$$+ \dots \quad \dots, \tag{51b}$$

evaluating only a few terms of the resulting series.

(vi) Let us integrate both sides of (47) between the limits 0 and θ $(< \tfrac{1}{2}\pi)$. Then

$$\int_0^{\theta} \frac{\sin\theta}{\theta} d\theta = \sin\theta \left[1 + \sum_{n=1}^{\infty} (-1)^n \frac{M_{2n}}{2n+1} (2\sin\theta)^{2n} \right]. \tag{52}$$

By comparing the series on the right-hand side when $\theta = \tfrac{1}{2}\pi$ with the convergent series $\Sigma \frac{1}{n^{3/2}}$. we see that the series is convergent for $\theta = \tfrac{1}{2}\pi$ as well. Hence putting $\theta = \frac{\pi}{2}$ in (52) we get

$$\int_0^{\pi/2} \frac{\sin\theta}{\theta} d\theta = 1 + \sum_{n=1}^{\infty} (-1)^n \frac{2^{2n}}{2n+1} M_{2n}. \tag{53}$$

14. The second definite integral involving F (x) is also due to Gauss and is defined by

$$K_{2p} = \frac{1}{(2p)!} \int_{-\frac{1}{2}}^{+\frac{1}{2}} x F_{2p-2}(x+p-1)\, dx$$

$$= \frac{1}{(2p)!} \int_{p-\frac{3}{2}}^{p-\frac{1}{2}} (x-p+1) F_{2p-2}(x)\, dx = \frac{1}{2p!} \int_{-\frac{1}{2}}^{+\frac{1}{2}} x^{[2p]} dx.$$

Since $F_{2p-2}(x+p-1)$ or $x^{[2p]-1}$ is an odd function of x,

$$\int_{-\frac{1}{2}}^{+\frac{1}{2}} F_{2p-2}(x+p-1)\, dx = 0 = \int_{p-3}^{p-\frac{1}{2}} F_{2p-2}(x)\, dx.$$

$$\text{Now, } F_{2p-1}(x) = (x-2p+1)\, F_{2p-2}(x)$$
$$= (x-p+1)\, \dot{F}_{2p-2}(x) - p\, F_{2p-2}(x).$$

Integrating between the limits $p-\frac{3}{2}$ and $p-\frac{1}{2}$, we get the following set of values from the first set.

$$K_{2p} = \frac{1}{(2p)!}\int_{p-\frac{1}{2}}^{p+\frac{1}{2}} F_{2p-1}(x)\, dx = \frac{1}{(2p)!}\int_{p-\frac{3}{2}}^{p-\frac{1}{2}} F_{2p-1}(x)\, dx$$

$$= \frac{1}{(2p)!}\int_{-\frac{1}{2}}^{+\frac{1}{2}} F_{2p-1}(x+p)\, dx = \frac{1}{(2p)!}\int_{0}^{1} x^{[2p+1]-1}\, dx.$$

Following the method of Art. 12 we obtain from the first integral

$$(2p)!\; K_{2p} = \frac{1}{2.2!} F_{2p-2}(p-\tfrac{1}{2}) - \frac{1}{2^2.3!} F'_{2p-2}(p-\tfrac{1}{2})$$

$$+ \frac{1}{2^3.4!} F''_{2p-2}(p-\tfrac{1}{2}) - \ldots \text{ to } 2p \text{ terms, whence}$$

$$K_{2p} = \frac{(-1)^{p-1}\,(2p-3)!}{2^{4p-3}p!\;(p-2)!}\Bigg[\frac{1}{2.2!}\left(1-\frac{1}{3(2p-1)}\right)$$
$$-\frac{2!}{2.4!}\left(1-\frac{3}{5(2p-1)}\right)\Sigma^{p-1}_{-1}$$
$$+\frac{4!}{2.6!}\times\left(1-\frac{5}{7(2p-1)}\right)\Sigma^{p-1}_{-2} - \ldots \text{ to } 2p \text{ terms,}\Bigg] \quad (54)$$

where Σ^{p}_{-r} stands for the sum of products, taken r at a time, of the reciprocals of squares of the first p odd natural numbers, *viz.*, 1, 3, 5, . . . $(2p-1)$. As will appear from the above, $p > 2$.

If we denote similar sums to infinity by the symbol Σ_{-r}, we shall have for large values of p

$$K_{2p} \sim \frac{(-1)^{p-1}}{2^{2p+2}\,\pi^{1/2}p^{3/2}}\left[1-\frac{2!}{2.4!}\Sigma_{-1}+\frac{4!}{2.6!}\Sigma_{-2}-\ldots\right]. \quad (54a)$$

But from trigonometry we have

$$\cos\frac{\pi\sqrt{x}}{2} = \left(1-\frac{x}{1^2}\right)\left(1-\frac{x}{3^2}\right) \ldots \text{ to infinity.}$$

Whence we obtain

$$\Sigma = \frac{\pi^{2r}}{2^{2r}.(2r)!}$$

With these values the series in square brackets on the right-hand side of (54*a*), become equivalent to

$$\frac{8}{\pi^2}\left(1-\cos\frac{\pi}{2}\right), \text{ or to } \frac{8}{\pi^2}.$$

Thus we obtain the known result (*cf.* Steffensen, *loc. cit.*, p. 109) :—

$$K_{2p} \sim \frac{(-1)^{p-1}}{2^{2p-1}\,\pi^{5/2}p^{3/2}}. \tag{55}$$

15. *Recurrence formulae for K's.*

(i) Let us integrate (38) between the limits 0 and 1. We shall then have, after division by (2*p*) ! and a little simplification,

$$\frac{2^{2p}-(2p+1)}{2^{2p}.(2p+1)!}=K_{2p}+\frac{a_{p,1}}{2^2.2p\,(2p-1)}K_{2p-2}$$
$$+\frac{a_{p,2}}{2^4.2p\,(2p-1)\,(2p-2)\,(2p-3)}K_{2p-4}+\ldots \text{ to } p \text{ terms}, \tag{56}$$

the last term of the series involving K_2.

(ii) Let us replace *p* in (41) by *p*—1, and integrate between the limits $-\frac{1}{2}$ and $+\frac{1}{2}$. On division by (2*p*) ! we get

$$\frac{1}{2^{2p}.\,(2p+1)!}=K_{2p}+\frac{c_{p-1,1}}{2p\,(2p-1)}K_{2p-2}$$
$$+\frac{c_{p-1,2}}{2p\,(2p-1)\,(2p-2)\,(2p-3)}K_{p2-4}+\ldots \text{ to } p \text{ terms}. \tag{57}$$

(iii) Next, we shall establish a new trigonometrical relation similar to (47).

Stirling's interpolation formula with remainder term is (*cf.* Steffensen, *loc. cit.*, p. 27) :—

$$f\,(x)=\sum_{n=o}^{p}\left[\frac{x^{[2n]-1}}{(2n-1)!}\square\,\delta^{2n-1}f\,(0)+\frac{x^{[2n]}}{(2n)!}\delta^{2n}f\,(0)\right]$$
$$+\frac{x^{[2p+2]-1}}{(2p+1)!}f^{2p+1}\,(\xi)\,, \tag{58}$$

it being understood that there should be no term which would contain (—1) !. Apply this formula to the function $f(x)=\cos\,(2\theta x)$, where θ is a constant to be chosen conveniently. This makes

$$\delta^{2n}f\,(0)=(-1)^n.\ (2\sin\theta)^{2n}. \tag{59}$$

Integrate both sides of (58), for this function, between the limits $-\frac{1}{2}$ and $+\frac{1}{2}$). Taking into consideration that

$$\int_{+a}^{-a}x^{[2n]-1}\,dx=0,$$

we get

$$\frac{\sin\theta}{\theta} = \sum_{n=0}^{p} (-1)^n K_{2n} (2\sin\theta)^{2n} + R', \tag{60}$$

where

$$R' = \int_{-\frac12}^{+\frac12} \frac{x^{[2p+2]-1}}{(2p+1)!} f^{2p+1}(\xi)\, dx \tag{61}$$

$$= \int_{-1/2}^{0} + \int_{0}^{\frac12} \frac{x^{[2p+2]-1}}{(2p+1)!} (-1)^{p+1} (2\theta)^{2p+1} \sin(2\theta\xi)\, dx$$

. . . . (61a)

The quantity $x^{[2p+1]-1}$ does not change sign in the interval $(-\frac12, 0)$, or in the interval $(0, +\frac12)$; and

$$\int_{-\frac12}^{0} x^{[2p+2]-1}\, dx = - \int_{0}^{\frac12} x^{[2p+2]-1}\, dx .$$

Further, sine of an angle does not exceed unity. Therefore, applying the Mean Value Theorem to each of the integrals of (61a) and taking them together, we get

$$R' \,| < 2 .\ (2\theta)^{2p+1} \left| \int_0^{\frac12} \frac{x^{[2p+2]-1}}{(2p+1)!}\, dx \right. \tag{62}$$

Since the maximum value of $F_{2p}(x+p)$, or $x^{[2p+2]-1}$ in the interval (0, 1) occurs beyond $x=\frac12$, (see the result at the end of (iii) of Art. 8), it is evident that

$$\left| \int_0^{+\frac12} \frac{x^{[2p+2]-1}}{(2p+1)!}\, dx < \frac12 \left| \int_0^{1} \frac{x^{[2p+2]-1}}{(2p+1)!}\, dx \right|, \textit{or} \left| \frac14 M_{2p} \right.\right.$$

from (27). Therefore,

$$| R' | < \frac{(2\theta)^{2p+1}}{2} \, | M_{2p} | . \tag{63}$$

Considering the asymptotic expression for $| M_{2p} |$, we see that for very large values of p

$$| R' | < \frac{2 . \theta^{2p+1}}{\pi^{3/2}\, p^{1/2}} . \tag{63a}$$

Hence $| R' | \longrightarrow 0$ when $p \longrightarrow \infty$, if $| \theta | \leqslant 1$. Thus we have for $| \theta | \leqslant 1$,

$$\frac{\sin\theta}{\theta} = 1 + \sum_{n=1}^{\infty} (-1)^n K_{2n} (2\sin\theta)^{2n}, \tag{64}$$

K_0 being unity.

Since K_2 is positive, K_4 negative, and so on alternately, every term of the series (64) is negative; and since the left-hand side is positive for the range of θ under consideration, the series under the summation sign must be less than unity.

D'Alembert's ratio-test will show that the series is convergent when $|\sin\theta| < 1$, or $|\theta| < \frac{\pi}{2}$. Further, when $|\theta| = \frac{\pi}{2}$, a comparison of this series with the convergent series $\Sigma \frac{1}{n^{3/2}}$, will show that the former is convergent too. Since (64) is true for a variable $|\theta|$, although $\leqslant 1$, it is clear that the right-hand side will continue to have $\frac{\sin\theta}{\theta}$ for its sum even when

$$1 < |\theta| \leqslant \frac{\pi}{2}$$

Let us put $\theta = \frac{\pi}{6}, \frac{\pi}{4}, \frac{\pi}{3}, \frac{\pi}{2}$ in (64). We shall then obtain

$$\frac{3}{\pi} = 1 - \sum_{n=1}^{\infty} |K_{2n}|,$$

$$\frac{2\sqrt{2}}{\pi} = 1 - \sum_{n=1}^{\infty} 2^n |K_{2n}|,$$

$$\frac{3\sqrt{3}}{\pi} = 1 - \sum_{n=1}^{\infty} 3^n |K_{2n}|,$$

and
$$\frac{2}{\pi} = 1 - \sum_{n=1}^{\infty} 4^n |K_{2n}|.$$

Finally if we put $\theta = \frac{1}{10}\pi$ and simplify, we get

$$\frac{5}{\pi} = \frac{\sqrt{5}+1}{2} - \sum_{n=1}^{\infty} \left(\frac{\sqrt{5}-1}{2}\right)^{2n-1} |K_{2n}|.$$

Also, on integrating (64) between the limits 0 and $\frac{1}{2}\pi$, we obtain the result [*cf.* (53)]:—

$$\int_0^{\pi/2} \frac{\sin\theta}{\theta}\, d\theta = \frac{\pi}{2}\left[1 - \sum_{n=1}^{\infty} \frac{2(2n-1)!}{n!\,(n-1)!} |K^{2n}|\right]. \tag{65}$$

(iv) Multiply both sides of (64) by θ and expand in powers of $\sin\theta$. Equating coefficients of $\sin^{2p+1}\theta$ we get after a little simplification,

$$\frac{(-1)^{p-1}}{2^{2p}} \cdot \frac{1.3.5\ldots(2p-1)}{2.4.6\ldots.\,2p} \cdot \frac{1}{2p+1} = K_{2p} - \frac{1^2}{2^2.3!}K_{2p-2} + \frac{1^2.3^2}{2^4.5!}K^{2p-4} - \ldots \text{ to } p \text{ terms}, \tag{66}$$

the known formula (*cf.* Steffensen, *loc. cit.*, p. 191).

(v) If we expand both sides of (64) in powers of θ, and equate coefficients of θ^{2p}, we shall have after cancelling common factors from both sides,

$$\frac{1}{2^{2p}(2p+1)!}=K_{2p}-\frac{b_{n,1}}{2^2}K_{2p-2}+\frac{b_{n,2}}{2^4}K_{2p-4}-\text{..to } p \text{ terms} \tag{67}$$

where the b's are given by (50).

(vi) Replace θ by 2θ in (64), and divide by $\cos\theta$. We shall then obtain

$$\frac{\sin\theta}{\theta}=\sec\theta+\sum_{n=1}^{\infty}(-1)^n K_{2n}(2\sin\theta)^{2n}\cos^{2n-1}\theta. \tag{68}$$

Equate the right-hand sides of (64) and (68); if we expand these in powers of $\sin\theta$, and compare the coefficients of $\sin^{2p}\theta$ from both sides of the new equation, we get on rearrangement,

$$\frac{(2^{2p}-1)}{2^{2p}}K_{2p}+\frac{(2p-1)}{2^5}K_{2p-2}+\frac{(2p-1)(2p-3)}{2^{10}.2!}K_{2p-4}$$
$$+\frac{(2p-1)(2p-3)(2p-5)}{2^{15}.3!}K_{2p-6}+\text{...... to } p \text{ terms}$$
$$=\frac{(-1)^p}{2^{6p}}\frac{1.3.5....(2p-1)}{p!}. \tag{69}$$

(vii) Again replace θ in (64) by 3θ. Since $\sin 3\theta = 3\sin\theta\,(1-\frac{4}{3}\sin^2\theta)$, we shall have

$$\frac{\sin\theta}{\theta}=(1-\tfrac{4}{3}\sin^2\theta)^{-1}+\sum_{n=1}^{\infty}(-1)^n K_{2n}(6\sin\theta)^{2n}\times$$
$$(1-\tfrac{4}{3}\sin^2\theta)^{2n-1}. \tag{70}$$

Thus the right-hand sides of (70) and (64) are equivalent.

Express both in power series of $\sin\theta$ and equate coefficients of $\sin^{2p}\theta$ from the results. After a little rearrangement we shall get

$$-\frac{3^{2p}-1}{3^{2p}}K_{2p}=\frac{(-1)^p}{3^{3p}}+\Big[{}^{2p-1}C_1\frac{K_{2p-2}}{3^3}+{}^{2p-1}C_2\frac{K_{2p-4}}{3^6}$$
$$+\text{.... to } 2p \text{ terms}\Big]. \tag{71}$$

16. *Relations between the* M's *and* K's.

(i) From (47) and (64) we get

$$1+\sum_{n=1}^{\infty}(-1)^n K_{2n}(2\sin\theta)^{2n}$$
$$=\cos\theta+\sum_{n=1}^{\infty}(-1)^n M_{2n}(2\sin\theta)^{2n}\cos\theta. \tag{72}$$

Express $\cos\theta$ in power series of $\sin\theta$, and equate coefficients of $(-1)^p(2\sin\theta)^{2p}$ from both sides. Then

$$K_{2p}=M_{2p}+\frac{1}{2^3}M_{2p-2}-\frac{1}{2^6.2!}M_{2p-4}+\frac{1.3}{2^9.3!}M_{2p-6}-\frac{1.3.5}{2^{12}.4!}M_{2p-8}+\ldots.+(-1)^p\frac{1.3.5.\ldots(2p-5)}{2^{3p-3}.(p-1)!}M_2-(-1)^p\frac{1.3.5.\ldots(2p-3)}{2^{3p}.\,p!}. \tag{73}$$

(ii) Differentiate (64) with respect to θ and multiply by $\frac{\theta}{\cos\theta}$; then

$$\left(1-\frac{\sin\theta}{\theta\cos\theta}\right)=\sum_{n=1}^{\infty}(-1)^n K_{2n}(2\sin\theta)^{2n-1}(4n\theta),$$ or, from (47),

$$\sum_{n=1}^{\infty}(-1)^{n+1}M_{2n}(2\sin\theta)^{2n}=\sum_{n=1}^{\infty}(-1)^n K_{2n}(2\sin\theta)^{2n-1}\times(4^n\theta). \tag{74}$$

Equate coefficients of $(-1)^p(2\sin\theta)^{2p}$, after expressing θ in powers of $\sin\theta$. We thus obtain

$$-M_{2p}=2pK_{2p}-\frac{p-1}{2^2.3}K_{2p-2}+\frac{p-2}{2^3.5}\cdot\frac{1.3}{2.4}K_{2p-4}-\ldots+(-1)^p\frac{1}{2^{2p-3}.(2p-1)}\cdot\frac{1.3\ldots.(2p-3)}{2.4\ldots.(2p-2)}K_2. \tag{75}$$

This relation shows that M_{2p} and K_{2p} have opposite signs and that $|M_{2p}|>2p|K_{2p}|$.

Multiply (66) by $(2p+1)$ and subtract (75) from the result. After transposing, we get the simpler formula

$$M_{2p}=\left[K_{2p}-\frac{1^2}{2^2.2!}K_{2p-2}+\frac{1^2.3^2}{2^4.4!}K_{2p-4}-\ldots\text{to } p \text{ terms}\right]+(-1)^p\frac{1.3.5\ldots.(2p-1)}{2.4.6\ldots.2p}. \tag{75a}$$

(iii) Divide (68) by $\cos\theta$ and use (47). Thus

$$1+\sum_{n=1}^{\infty}(-1)\,M_{2n}(2\sin\theta)^{2n}=\sec^2\theta+\sum_{n=1}^{\infty}(-1)^n K_{2n}(2\sin\theta)^{2n}\cos^{2n-2}\theta. \tag{76}$$

Expand the right-hand side in power series of sin θ and equate coefficients of $(-1)^p$ $(2 \sin \theta)^{2p}$ from both sides. We get after division by 2^{2p},

$$M_{2p} = \frac{(-1)^p}{2^{2p}} + 2^{2p}\left[K_{2p} + \frac{p-1}{2^4} K_{2p-2} + \frac{(p-1)\,(p-2)}{2^8 . 2\,!} K_{2p-4} + \ldots \text{ to } p \text{ terms}\right]. \quad (77)$$

17. The third definite integral involving F_n (x) is associated with Laplace's summation formula, and is defined as (*cf.* Steffensen, *loc. cit.*, pp. 104-107) :—

$$L_p = \frac{1}{p\,!} \int_0^1 F_{p-1}\,(x)\,dx = \frac{1}{p\,!} \int_0^1 x^{(p)}\,dx\;. \qquad (78)$$

A recurrence formula in the L's is easily derived by the consideration of the integral $\int_0^1 (1+t)^x \; dx$. Its asymptotic expression for large values of p is given by

$$L_p \backsim \frac{(-1)^{p+1}}{p \log^2 p}\,.$$

When p is very large, we have from (27) and (37)

$$q_{2p} \quad \text{or} \quad \left|\frac{L_{2p}}{M_{2p}}\right| \backsim \frac{2^{2p-2}\ \pi^{3/2}}{p^{1/2} \log^2 (2p)}\;,$$

and

$$q_{2p+1} \text{ or } \left|\frac{L_{2p+1}}{M'_{2p}}\right| \backsim \frac{2^{2p-1}\ \pi^{3/2}}{p^{1/2} \log^2 (2p+1)}\,. \qquad (79)$$

18. From the definition of K_{2p} (*cf.* Art. 14), it is evident that

$$K_{2p} = \frac{2}{(2p)\,!} \int_0^{1/2} x^{[2p]} dx = \frac{2}{(2p)\,!} \int_{p-1}^{p-\frac{1}{2}} (x - p + 1)\ F_{2p-2}\,(x)\ dx.$$

But the second integral $= (\bar{x} - p + 1)$ A, (80)

where A is the area under the curve $y = F_{2p-2}$ (x), from $x = p-1$ to $x = p - \frac{1}{2}$, and $\bar{x}$ the abscissa of the mean centre of this area. Let us define

$$\sigma_{2p-2} = \frac{A}{(2p-1)!} = \frac{1}{(2p-1)\,!} \int_{p-1}^{p-\frac{1}{2}} F_{2p-2}\,(x)\ dx. \qquad (81)$$

The integral is also equal to

$$-\int_{p-\frac{1}{2}}^{p-1} F_{2p-2}\,(x)\ dx = \int_0^{\frac{1}{2}} x^{[2p]-1} dx = -\int_{-\frac{1}{2}}^{0} x^{[2p]-1}\,dx.$$

We have already come across this integral in (62). Other forms for it can be easily written as has been done in the case of K_{2p}. Putting $(p+1)$ for p and calculating the integral last written, we get on simplification,

$$\sigma_{2p} = \frac{(-1)^p \ (p!)^2}{2^3 . \ (2p+1)!}\Big[1 - \frac{1}{2^2 . 2} S^p_{-1} + \frac{1}{2^4 . 3} S^p_{-2}$$

$$- \frac{1}{2^6 . 4} S^p_{-3} + \dots \text{to } p+1 \text{ terms}\Big]. \quad (82)$$

The first few σ's are :

$$\sigma_0 = \tfrac{1}{8} ; \ \sigma_2 = -\frac{7}{384} ; \ \sigma_4 = \frac{163}{46080} ; \ \sigma_6 = -\frac{4633}{6193152} ;$$

$$\sigma_8 = \frac{1847633}{11147673600} .$$

When p is very large, $\sigma_{2p} \backsim \frac{(-1)^p \pi^{\frac{1}{2}}}{2^{2p+4} \ p^{\frac{1}{2}}}\Big[1 - \frac{1}{4 . 2} S_{-1}$

$$+ \frac{1}{4^2 . 3} S_{-2} \dots \Big] = \frac{(-1)^p}{2^{2p+1} \ \pi^{3/2} \ p^{\frac{1}{2}}} , \text{ or } \tfrac{1}{4} M_{2p}. \quad (83)$$

19. Let us find the abscissa of the mean centre of the area under the curve $y = F_{2p}\ (x)$ from $x = p$ to $x = p+1$. We might introduce a new integral in this connection, *viz.*,

$$D_{2p+1} = \frac{1}{(2p+1)!}\int_{p}^{p+1} (x - p - \tfrac{1}{2}) \ F_{2p}(x) \ dx$$

$$= \frac{1}{(2p+1)!} \quad (\bar{x}' - p - \tfrac{1}{2}) \ A' ,$$

$$= \frac{1}{(2p+1)!} \int_{-\frac{1}{2}}^{+\frac{1}{2}} (x + p + \tfrac{1}{2}) \ x^{[2p+1]} \ dx , \quad (84)$$

where $\bar{x}'$ is the abscissa of the mean centre and A′ the area under question. $A' = M'_{2p} \ (2p+1)!$, or $\frac{1}{2} M_{2p} \ (2p+1)!$. Therefore

$$D_{2p+1} = \tfrac{1}{2}(\bar{x}' - p - \tfrac{1}{2}) \ M_{2p}. \quad (84a)$$

When $p \longrightarrow \infty$, the area tends to become symmetrical about the ordinate at the mid-point, *viz.*, the point $x = p + \frac{1}{2}$, and hence $\bar{x}'$ tends to $p + \frac{1}{2}$.

Since $x^{[2p+1]}$ is an odd function of x, its integral between the limits $-a$ to $+a$ would be zero, and hence

$$D_{2p+1} = \frac{1}{(2p+1)!} \int_{-\frac{1}{2}}^{+\frac{1}{2}} x . \ x^{[2p+1]} \ dx, \quad (84b)$$

$$= \frac{1}{(2p+1)!} \int_{-\frac{1}{2}}^{+\frac{1}{2}} \left[x^{[2p+3]-1} + \frac{(2p+1)^2}{4} x^{[2p+1]-1} \right] dx$$

$$= (2p+2)\ M_{2p+2}\ + \tfrac{1}{2}(2p+1)\ M_{2p}. \tag{85}$$

Therefore,

$$\bar{x}' - p - \tfrac{1}{2} = 4(p+1) \frac{M_{2p+2}}{M_{2p}} + \tfrac{1}{2}\ (2p+1)\ , \tag{86}$$

which tends, when p is very large, to 0 (see above).

It can be shown by evaluating (84b) that

$$D_{2p+1} = \frac{(-1)^p\ (2p-1)!}{2^{4p+1}\ p!\ (p-1)!\ (2p+1)} \Bigg[\tfrac{1}{3} - \tfrac{1}{5} \Sigma^{p}_{-1} + \tfrac{1}{7} \Sigma^{p}_{-2}$$

$$- \tfrac{1}{9}\ \Sigma^{p}_{-3} + \dots \text{ to } p+1 \text{ terms} \Bigg]. \tag{87}$$

The first few D's are as follow :

$$D_1 = \frac{1}{12} = 2K_2;\ D_3 = -\frac{1}{720} = \frac{8}{17}\ K_4\ ;$$

$$D_5 = \frac{1}{6720} = \frac{144}{367}\ K_6;\ D_7 = -\frac{1891}{87091200} = \frac{30256}{82577}\ K_8.$$

Also, for large values of p,

$$D_{2p+1} \backsim \frac{(-1)^p}{2^{2p+2}\ \pi^{3/2}\ p^{3/2}} \left(1 - \frac{8}{\pi^2}\right)$$

$$\backsim \frac{\pi}{2} \left(1 - \frac{8}{\pi^2}\right) K_{2p+2}\ , \tag{88}$$

or, $\frac{1}{\pi}\ \ K_{2p+2}$ nearly, if we take $\pi^2 = 10$ approximately.

20. From a comparative study of recurrence formulæ (48) and (66) for M_{2p}'s and K_{2p}'s, it is clear that any linear combination of the two will also satisfy similar recurrence formula except for the constant term on the left-hand side. The coefficients occurring in the linear combination should, however, be independent of p. The quantity D_{2p+1} cannot therefore satisfy such a formula, but if we introduce another quantity, say

$$\sigma'_{2p} = K_{2p} - \tfrac{1}{2}\ M_{2p}\ , \tag{89}$$

it will. In fact, we shall have

$$\frac{(-1)^{p+1}}{2^{2p}} \; \frac{1.3.5. \; \ldots \; (2p-1)}{2.4.6. \; \ldots\ldots \; 2p} \; \frac{p+1}{2p+1}$$

$$= \sigma'_{2p} - \frac{1^2}{2^2.3!} \sigma'_{2p-2} + \frac{1^2.3^2}{2^4.5!} \sigma'_{2p-4} - \qquad \ldots\ldots \qquad (90)$$

The quantity σ'_{2p} $(2p)!$ represents the area under the curve $y = F_{2p-1}(x)$ from $x = p$ to $x = p + \frac{1}{2}$. It is also equal to the definite integral

$$\int_{\frac{1}{2}}^{1} x^{[2p+1]-1} \; dx.$$

However, recurrence formulæ for D_{2p+1} can be easily obtained, either independently, or with the help of the relation (85).

(*To be continued*)

RAJARAM COLLEGE,
KOLHAPUR

THE PRODUCT OF ANY TWO DEMLO-NUMBERS

An Approach to the General Theory

By

PROFESSOR M. L. CHANDRATREYA, M.A.,

AND

D. R. KAPREKAR, B.SC., S.T.C.

(1) SOME particular types of products of Demlo-numbers have been already discussed elsewhere ; *e.g.*, the Product of Super-wonderful Demlo-numbers in March 1942 and a case of the product of two Demlo-numbers in November 1942, and product of some Linear Demlo-numbers in November 1939. We are now in a position to take up the product of any two Demlo-numbers of any type and any length. In this article it is proposed to give a genesis of such products and an approach to their determination.

(2) It has been pointed (B. U. J. March 1942) that $\frac{M}{81}$ has recurring periods consisting of 9, 3, or 1 digits, where M is any number < 81. The following two theorems in connection with these recurring figures of M can be easily seen to be true.

Theorem I. Take the recurring digits of $\frac{M}{81}$, again and again. Take also the same cycle of digits beginning at some other digit in the former sum. Subtract the smaller from the bigger and the difference is a number consisting of the same single digit repeated. Thus

$$\frac{17}{81} = .209876543$$

Take this cycle 209876543209876 ....
and another, say, beginning at 8, 876543209876 ....
subtracting the smaller from the bigger,

$$\begin{array}{r} 876543209876 \\ 209876543209 \\ \hline 66666666666.7. \end{array}$$

We see that the same digit 6 is repeated. Even if the greater is subtracted from the smaller thus

$$\begin{array}{r} 209876543209 \\ 876543209876 \\ \hline 333333333333 \end{array}$$

the same digit 3 is repeated. This is true for any value of M whether the recurring period is of 9 digits or 3 or 1.

Theorem II. This is just a converse of Theorem I. If we write any digit repeated K times and subtract from this number the period of $\frac{M}{81}$, the result of subtraction is the period of some other number $\frac{M'}{81}$. Symbolically $(r)_n - \frac{M}{81} = \frac{M'}{81}$. Thus, for example, take $r=8$ and $M=37$. Then

$$\frac{37}{81} = .456790123$$

And therefore

$$\begin{array}{r} 88888888888 \\ 45679012345 \\ \hline 43209876543\cdots\cdots \end{array}$$

The subtraction gives $.\dot{4}3209876\dot{5} = \frac{35}{81}$

(3) It has been shown (B. U. J. November 1940) that the product of two non-similar Demlo-numbers M $(r)_n$ P and M′ $(r')_{n'}$ P′ reduces to

$$\frac{G}{81} \times \left(10^{n+n'}-1\right)\left(10^{n'+n'_1}\ 1\right)$$

Where $G=(9M+r)\ (9M'+r')$ and $(9M+r)$ and $(9M'+r')$ are the demlofiers of the two given numbers while $n+n_1$ and $n^1+n^1_1$ are their lengths. We shall bring out the peculiarities by considering a few numerical examples.

(4) *Example I.* $15\ (4)_8\ 29 \times 19\ (5)_5\ 36$

The demlofiers of the two numbers are $15 \times 9 + 4 = 139$ and $19 \times 9 + 5 = 176$

$\therefore\ 15\ (4)_8\ 29 = 139 \times (1)_{10}$ and $19 (5)_5\ 36 = 176 \times (1)_7$

Hence the product $= 139 \times 176 \times (1)_{10} \times (1)_7$

$$= 24464 \times \left(\frac{10^{10}-1}{9'}\right) \times \left(\frac{10^7-1}{9}\right)$$

$$= 302\ \tfrac{2}{81} \times \left(10^{10}-1\right)\left(10^7-1\right)$$

$$= 302\ \tfrac{2}{81} \times \left(10^{17}-10^{10}-10^7+1\right)$$

arranging the powers of ten always in descending order. Here

$$\frac{2}{81} = .\dot{0}2469135\dot{8}\ldots\ldots\ldots$$

Thus 302.024691358...... is to be multiplied by the bracketed quantity $(10^{17}-10^{10}-10^{7}+1)$. Multiplying by 10^{17} means only shifting the decimal point 17 places further down when the cycle of figures is repeated. Similar interpretation being given to the other products by 10^{10}, 10^{7} and 1. The combined work is shown below in four lines.

$$\begin{array}{lr}
+ & 30202469135802469135.802469\ldots\ldots\ldots\text{(i)}\\
- & 3020246913580.2469\ldots\ldots\ldots\ldots\text{(ii)}\\
- & 3020246913.2802\ldots\ldots\ldots\ldots\text{(iii)}\\
+ & 302.0246\ldots\ldots\ldots\ldots\text{(iv)}
\end{array}$$

The first and last lines are positive and the 2nd and 3rd are negative.

(5) We shall obtain the result step by step. In subtracting (ii) from (i) we have the application of Theorem I except for the first few figures. The difference is

$$30202466115555555555.5555\ldots\ldots\ldots\text{(v)}$$

Subtracting (iii) from this result and applying Theorem II, thus

$$\begin{array}{r}
3020246611555|5555555.5555\ldots\ldots\\
302|0246913.5802\ldots\ldots\\
\\
3020246611253|5308641.9753\ldots\ldots\ldots\text{(vi)}
\end{array}$$

The new period is 530864197 and this is repeated again and again.

Adding (iv) to this quantity

$$\begin{array}{r}
3020246611253|5308641.9753086\ldots\ldots\ldots\\
302.0246913\ \ldots\ldots\\
\hline
3020246611253|5308943.9999999\ldots\text{(vii)}
\end{array}$$

Putting $.9999\ldots\ldots=1$, we get the whole product required
3020246611253|5308|944

The point to be noted is that the result ultimately is written as an integer even though the process is carried on in decimals. In every case the figures after the decimal point ultimately are 9s repeated, the equivalent value being taken as 1.

(6) *Example II.* $15\,(4)_{12}29\times 19(5)_{5}36$

$$= 139\times 176\times (1)_{14}\times (1)_{7}$$

$$24464\times\left(\frac{10^{14}-1}{9}\right)\times\left(\frac{10^{7}-1}{9}\right)$$

$$302.\dot{0}2469135\dot{8}\times\ (10^{21}-10^{14}-10^{7}+1)$$

The following will show the work that is done in this connection.

$$\begin{array}{lr}
+ & 302|0246913|5802|469|1358024.69135802\ldots\ldots\ldots\ldots(\mathrm{i})\\
- & 302|0246|913|5802469.1358024\ldots\ldots\ldots\ldots(\mathrm{ii})\\
- & |302|0246913.580246\ldots\ldots\ldots\ldots(\mathrm{iii})\\
+ & 302.024691\ldots\ldots\ldots\ldots(\mathrm{iv})
\end{array}$$

(i) — (ii) gives

$$302|024661\,1|55555555555555\cdot555\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(\mathrm{v})$$

(v) — (iii) gives

$$302|024661\,1|\underline{5555}|2535308641\cdot97539\ldots\ldots\ldots\ldots\ldots\ldots\ldots(\mathrm{vi})$$

(vi) + (iv) gives

$$302|024661\,1|5555|2535308943\cdot99999\ldots\ldots\ldots\ldots\ldots\ldots\ldots(\mathrm{vii})$$

Hence

$$302|024661\,1/5555|253308944\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(\mathrm{viii})$$

is the required product.

The answers of Examples I and II differ only by the repetition o. the digit 5 occurring in the middle part four times.

(7) A few observations will be made with respect to the processf The 302 in every line will be referred to as the integer and the remaining part as the decimal of that line. While subtracting line (ii) from (i) we have to subtract 302.0246......from the above line. The process of subtraction does not give any carrying of one when 302 are being subtracted from the above line. This fact we shall indicate by saying that the integer in line (ii) has a zero type. The integer in line one remains unaffected while the integer in line two may or may not remain unaffected. When it is affected by carrying one in the process of subtraction, we shall say that it is of + type. In the example we have taken, the integer in line (ii) is of zero type as already indicated.

Now consider the next result of subtracting line (iii) from (v). Here again while subtracting 302, the integer from the above figure, there is no carrying of one from the previous digits and this integer in line (iii) is also of zero type.

It now only remains to add line (iv) to the result so obtained. After the addition the decimal part is always .9999....which we take to be equivalent to 1. This means that the figures after the decimal points may be dropped out altogether and the result compensated for by adding 1 to 302 of that example. In view of the integers in line (ii) and (iii) not being affected in the example taken, we shall call that product as of (0, 0) type. The behaviour of integers in lines (i) and (iv) has been already described above.

(8) *Example* III is added to bring out the necessary details once more.

$$25\ (8)_2\ 63\times18(4)_5\ 26=233\times166\times(1)_4\ \times(1)_7$$

$$=38678\times\frac{10^4-1}{9}\times\frac{10^7-1}{9}=477\frac{41}{81}\times(10^{11}-10^7-10^4+1)$$

$$=477\cdot\dot{5}0617283\dot{9}\times(10^{11}-10^7-10^4+1)$$

Therefore writing the four lines

$$\begin{array}{lr}
+ & 477\vert 5061\vert 7283\vert 950.617283\ldots\ldots\ldots\text{(i)} \\
- & 477\vert 5061\vert 728.395061\ldots\ldots\ldots\text{(ii)} \\
- & \vert 4775\vert 061.728395\ldots\ldots\ldots\text{(iii)} \\
+ & \vert 477.506172\ldots\ldots\ldots\text{(iv)}
\end{array}$$

$$\text{Hence} \qquad 477\vert 4584\vert 2222222\ldots\ldots\ldots\text{(v)}$$

While obtaining this, there was no carrying of one for the integer 477 of line (ii). While subtracting (iii) from this result (v), one has to be carried to the integer of line (iii). Hence this case of the product may be designated as (0, +) type. Thus it appears that the product of any two Demlo-numbers has one of the four types :

$$(0,\ 0),\ (+,\ +),\ (+,\ 0),\ \text{or}\ (0,\ +)$$

It is unnecessary to take products to represent these different types for illustration. An example of (+, +) type only is given below.

(9) $15\,(3)_5\,18 \times 13\,(5)_9\,42 = 138 \times 122 \times (1)_7 \times (1)_{11}$

$$= \frac{16836}{81} \times (10^{11}-1) \times (10^7-1) = 207\frac{69}{81} \times (10^{18}-10^{11}-10^7+1)$$

$$= 207.\dot{8}5\dot{1} \times (10^{18}-10^{11}-10^7+1)$$

$$\begin{array}{llr}
\text{Thus} & + & 207\vert 85185185185\vert 5185\vert 1851.851\ldots\ldots\ldots\text{(i)} \\
 & - & 207\vert 8517\vert 5185.185\ldots\ldots\ldots\text{(ii)} \\
 & - & \vert\ 207\vert 8518.518\ldots\ldots\ldots\text{(iii)} \\
 & + & \vert\ 207.851\ldots\ldots\ldots\text{(iv)}
\end{array}$$

While subtracting (ii) from (i), one has to be carried over and the integer is + type. The third line integer is to be subtracted from 6666 ....and here again one has to be carried over and the integer of the third line is also of + type. Thus the case taken represents the product (+, +) type.

(10) From the Examples and Theorems given up to now it will be seen that the product of any two Demlo-numbers has the following main factors.

The integer Q in $\frac{Q}{81}$ and remainder R with the recurring period of $\frac{R}{81}$ must be found. While subtracting line (iii) from (v) another period $\frac{R'}{81}$ appears as a consequence of Theorem II, where R and R′ and consequently their periods must have some relation between them. Moreover we have to consider the positions of the integers in different lines and the type to which the product belongs. It is also necessary to add one at the end in cancellation of the quantity .999......Finding these various quantities and thus getting a formula for the product of any two Demlo-numbers will form material of the next discussion.

(I have to thank the University of Bombay for the research grant given to me for conducting these researches.—D. R. KAPREKAR.)

COLLEGE OF ENGINEERING, POONA
KHARE'S WADA, DEOLALI

THE VALUE OF θ APPEARING IN THE LAGRANGE'S FORM OF THE REMAINDER

By

G. K. HEBALKAR

THE following question was asked in the B. A. (Hons.) essay paper of 1939 " . . . Hence obtain Taylor development for a function with Lagrange's form of the remainder $R_n = \frac{h^n}{\underline{|n}} f^n (a+\theta h)$. If the θ appearing in R_n above be considered a function of h, show that—

$$(i) \quad \theta \longrightarrow \frac{1}{n+1} \qquad \text{as } h \longrightarrow o;$$

$$(ii) \quad \left(\theta - \frac{1}{n+1}\right) \Big/ h \longrightarrow \frac{n}{2\,(n+1)^2(n+2)} \, \frac{\overset{n+2}{f}(a)}{\overset{n+1}{f}(a)}$$

if $\overset{n+2}{f}(x)$ is continuous in $(a,\ a+h)$ and $\overset{n+1}{f}(a) \mp 0$."

Principal Mahajani of Fergusson College also has worked out the above problem in the 3rd edition of his book "Lessons in Elementary Analysis." He too assumes the continuity of $\overset{n+2}{f}(x)$ to establish the result. Is it really needed ?*

As regards result (i) I have nothing new to say. So I agree that $\theta = \frac{1}{n+1}$, is a first approximation. If now $\overset{n+2}{f}(a)$ exists, we can write :—

$$f\,(a+h) = f\,(a) + \frac{h}{\underline{|1}} f^1(a) + \ldots \frac{h^{n+1}}{\underline{|n+1}} \overset{n+1}{f}(a) + \frac{h^{n+2}}{\underline{|n+2}} \left[\overset{n+2}{f}(a) + \beta\right]$$

where $\beta \longrightarrow o$ as $h \longrightarrow o$.

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* Referring to the latest edition of Hardy the reader will find that result (i) is usually proved under the assumption of Continuity of $f^{n+1}(x)$, [Hardy pp. 288,289] and result (ii) is stated under the assumption of Continuity of $f^{n+2}(x)$, [Hardy p. 332]. In *both* Cases Continuity is not needed. Principal Mahajani himself has pointed out in his book (page 143) how the condition can be sharpened by the use of young's theorem with reference to the result (i).—Ed.

[For this form of Young's Theorem readers should refer to Hardy's Pure Mathematics, art. 151].

Comparing the above result with—

$$f(a+h)=f(a)+\frac{h}{\underline{|1}}f^{1}(a)+\dots+\frac{h^{n}}{\underline{|n}}f^{n}(a+\theta h),\text{ we get}$$

$$\frac{h^{n}}{\underline{|n}}f^{n}(a+\theta h)=\frac{h^{n}}{\underline{|n}}f^{n}(a)+\frac{h^{n+1}}{\underline{|n+1}}f^{n+1}(a)+\frac{h^{a+2}}{\underline{|n+2}}\left[f^{n+2}(a)+\beta\right]$$

Applying Young's form to L. H. S., this gives on simplification :—

$$f^{n}(a)+\theta h f^{n+1}(a)+\frac{\theta^{2}h^{2}}{\underline{|2}}\left\{f^{n+2}(a)+\alpha\right\}=f^{n}(a)+\frac{h}{(n+1)}f^{n+1}(a)+\frac{h^{2}}{(n+1)(n+2)}\left[f^{n+2}(a)+\beta\right]$$

where $\alpha \longrightarrow o$, as $h \longrightarrow o$, which further simplifies into—

$$\theta f^{n+1}(a)+\frac{\theta^{2}h}{2}\left\{f^{n+2}(a)+\alpha\right\}=\frac{f^{n+1}(a)}{n+1}+\frac{h}{(n+1)(n+2)}\left[f^{n+2}(a)+\beta\right]$$

Now let $\theta=\frac{1}{n+1}+\theta'$ be a better approximation. Then θ' is small and its squares may be neglected. Also α, $\beta \longrightarrow o$ as $h \longrightarrow o$ and $\therefore$ are infinitesimals. Neglect then the terms in $h\alpha$, $h\beta$ and $h\theta'$ in comparison to terms in h. The above result then gives :—

$$\theta' f^{n+1}(a)-\frac{h f^{n+2}(a)}{2(n+1)^{2}}=\frac{h}{(n+1)(n+2)}f^{n+2}(a)$$

$$\theta'=\left[\frac{h f^{n+2}(a)}{(n+1)(n+2)}-\frac{h f^{n+2}(a)}{2(n+1)^{2}}\right]\div f^{n+1}(a)$$

$$=\frac{n\,h}{2(n+1)^{2}(n+2)}\,\frac{f^{n+2}(a)}{f^{n+1}(a)}$$

giving the desired result. I have not used the continuity of $f^{n+2}(x)$ at all.

WADIA COLLEGE,
POONA.

STUDIES IN EDUCATIONAL STATISTICS: V

Matriculation Examination 1941—University of Bombay

By

R. P. SHINTRE

(Use of research grant from the Bombay University was made in collecting and tabulating the data).

IN the Studies in Educational Statistics : 0, published in the *Journal of the University of Bombay* of March 1942, reference was made to the distribution of Matriculation totals for 1941, indicating various ways in which they may be studied.

The Matriculation Examination is held once every year by the Bombay University as its entrance examination. The heads of passing at present are : 1. English, 100 marks, one paper. 2. A second language* and a vernacular†, 200 marks, two papers. 3. History and Geography 100 marks, one paper. 4. Mathematics, 200 marks, two papers. And 5. Science‡, 100 marks, one paper. Total 700 marks.

The examination is held simultaneously at centres fixed by the University, the same papers being set. In 1941 it was held at the following centres : 1 Bombay, 2 Dadar, 3 Nasik, 4 Poona, 5 Kolhapur, 6 Sholapur, 7 Sangli, 8 Dhulia, 9 Dharwar, 10 Belgaum, 11 Bijapur, 12 Ahmedabad, 13 Baroda, 14 Surat, 15 Anand, 16 Rajkot, 17 Bhavnagar, 18 Karachi, 19 Hyderabad and 20 Shikarpur. Centres 1 to 3 lie in the Konkan group, 4 to 8 in the Deccan group, 9 to 11 in the Karnatak group, 12 to 17 in the Gujarat group and 18 to 20 in the Sind group.** A candidate may appear at any centre for the examination, but in most cases pupils in a school appear at the nearest centre. In 1941, 573 schools sent 26,883 pupils for the examination out of whom 13,511, *i.e.*, 50.3 per cent. passed.

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* One of : Sanskrit, Pali, Ardhamagadhi, Avesta-Pahlavi, Arabic, Persian, Latin, Greek, Hebrew, French, German, Portuguese, Spanish and Italian.

† One of : Marathi, Gujarati, Kannada, Tamil, Telugu, Bengali, Sindhi, Urdu, Hindi, and English.

‡ One of ; General Science, Physics and Chemistry, Botany and Zoology, Domestic Science and Physiology—Hygiene.

** Although Sind is politically separate, its schools and colleges are still affiliated to the Bombay University.

To pass the examination a candidate has to score at least 35 per cent. of the maximum marks in every head. If a candidate fails to pass the examination he is allowed, at his option, exemption from appearing again in those subject-heads in which he has scored at least 50% of the maximum marks. Candidates have the option of answering all papers except the paper in English either in English or in any of the vernaculars. This option was given from 1937 before which it was allowed only for the second language paper. · The table below shows how the candidates are exercising the option.

Table Showing Percentages of Candidates Answering the Papers in English and One of the Vernaculars

Percentage of Candidates Answering

	1937		1938		1939		1940		1941	
	Eng.	Ver.	Eng.	Ver.	Eng.	Vor.	Eng.	Ver.	Eng.	Ver.
2nd Language	23.71	76.29	21.10	78.90	16.55	83.45	12.64	87.36	12.86	87.14
History	31.46	68.54	28.06	71.94	22.80	77.20	19.24	80.76	17.18	82.82
Geography	31.46	68.54	30.19	69.81	26.67	73.33	21.68	78.32	19.58	80.42
Science ..	88.04	11.96	83.50	16.50	68.78	31.22	62.42	37.58	54.37	45.63
Mathematics	99.89	0.11	99.85	0.15	99.51	0.49	99.16	0.84	99.18	0.82

This clearly shows how an increasing number is taking advantage of the option of answering in the vernaculars in all the subjects. The smaller numbers in Science and in Mathematics appear to be due partly to the lethargy of our teachers in adapting words and expressions in the vernaculars for technical terms in these subjects.

The passing of the examination qualifies the candidates for admission to any of the colleges affiliated to the Bombay University. But in colleges where admissions are limited selection is made by the total marks obtained in the examination by the candidates. Although the number of candidates passing the examination is increasing, the number entering the colleges not only does not increase in the same proportion but is relatively falling as will be seen from the table given below.

Table Showing the Number Passing the Matriculation in Any Year and that Appearing for the First Year Examination in Colleges the Next Year and the Percentage of the Latter to the Former.

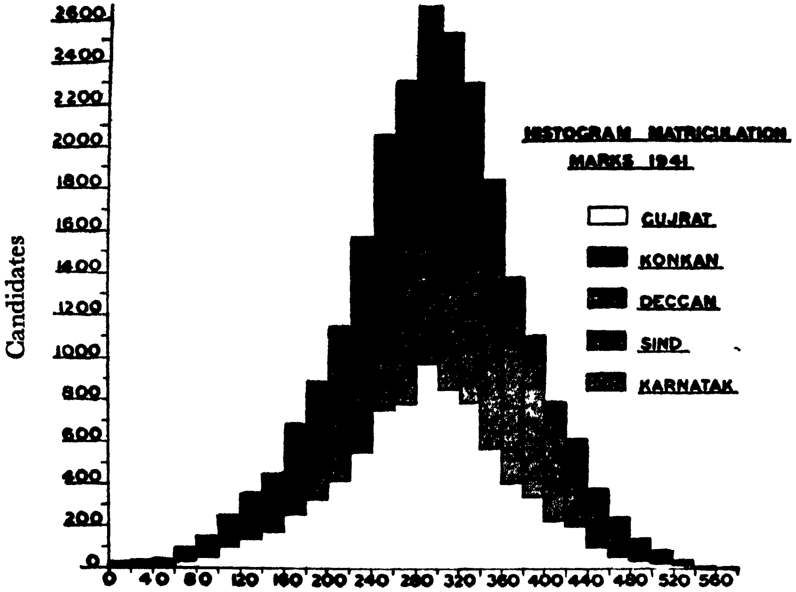
Year	No. passing Matric (i)	No. appearing F. Y. (ii)	Percentage of (ii) to (i)
1916	2339	2695	115.22
1917	1874	2300	122.73
1918	2934	2728	92.98
1919	2470	2598	105.18
1920	2952	2268	76.83
1921	2802	2550	91.01
1922	3616	3196	88.38
1923	4322	3636	84.13
1924	4362	3782	86.70
1925	3912	3604	92.12
1926	3403	3208	94.27
1927	4121	3309	80.29
1928	4165	3341	80.21
1929	6780	4501	66.38
1930	4391	3379	76.95
1931	7974	5201	65.22
1932	5806	4588	79.02
1933	7639	5065	66.30
1934	8747	5674	64.87
1935	7014	4953	70.61
1936	6725	4676	69.53
1937	8330*	4474	53.71
1938	10040	5707	56.84
1939	13332	7192	53.94
1940	11892	7119	59.86

Besides qualifying for admission to the University courses it also qualifies candidates for services of a lower grade except the menial grade. But whether those who do not enter the colleges are all absorbed in the services or how many of them take to other lines cannot be ascertained.

It is universally acknowledged that if the abilities of candidates are to be judged by this examination, it must be done by total marks obtained by them in the examination. In what follows, therefore, only the total marks obtained by the candidates who appeared in 1941 for the whole examination (*i.e.*, without taking advantage of the right of exemption earned in any subject) whether they passed or failed. Among those who failed there may be some who only submitted blank answer-books or who appeared only for some papers and did not appear for the remaining for one reason or another.

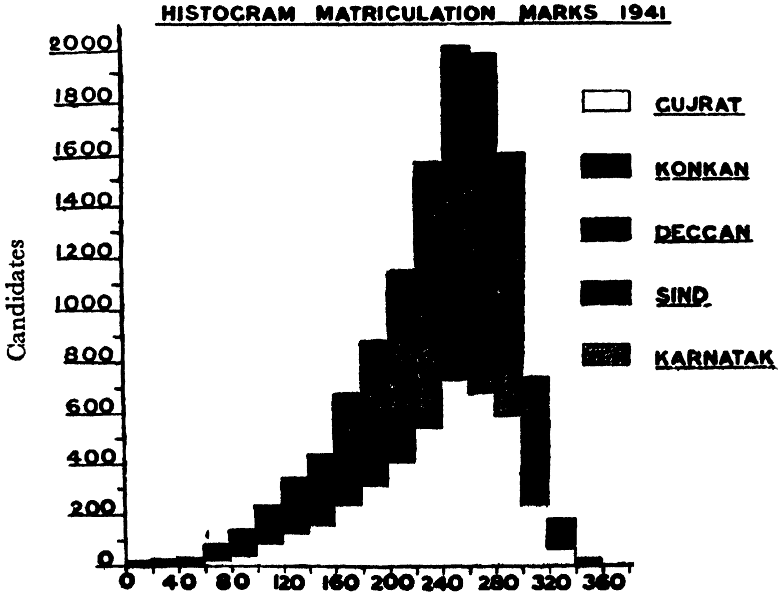
The following histograms will indicate the distribution of these totals. Fig. 1 is the layered histogram of the totals of all candidates, the number of candidates appearing at centres of the different groups being indicated by the layers.

This includes 2,983 passed in the supplementary examination held in November 1936.



Marks
Fig. 1

Figures 2 and 3 are similar histograms of the totals of candidates who failed and passed respectively.



Marks
Fig. 2

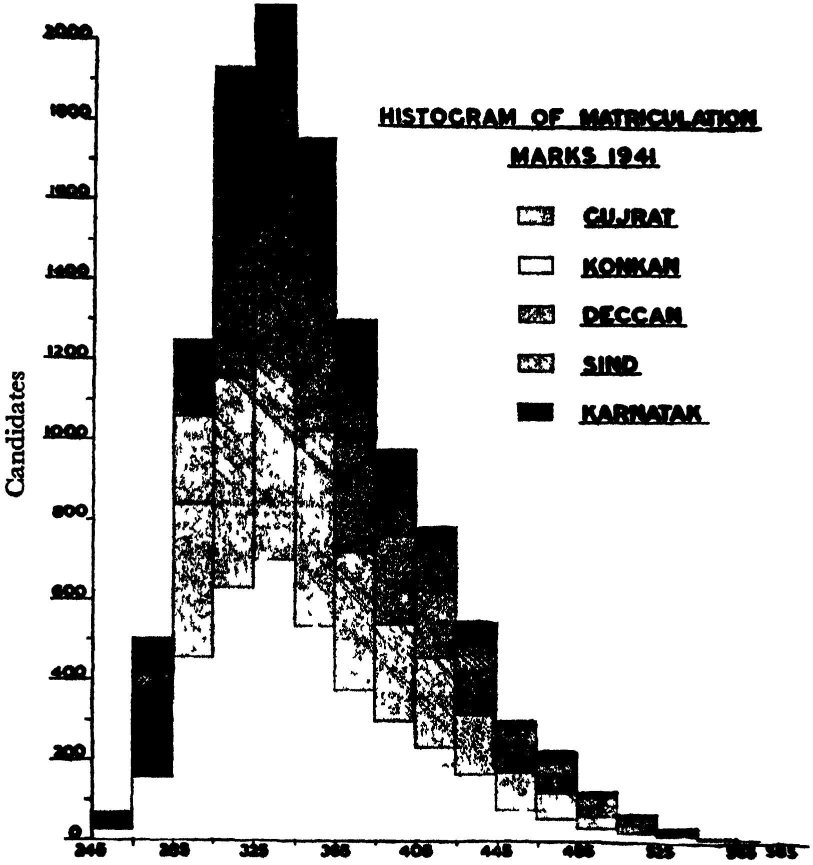


Fig. 3

The following table shows the ranking, by means, of the different examination centres and also of the groups of these centres according to University classification.

Ranking of Matriculation Centres

Mean marks	Sind 307.6	Deccan 300.3	Konkan 296.1	Gujarat 289.1	Karnatak 287.1
311.0		Sangli			
309.0	Hyderabad				
308.5	Karachi				
304.3		Poona			
302.2				Bhavnagar	
302.2	Shikarpur				
301.6				Surat	
301.2		Sholapur			
297.8			Nasik		

Ranking of Matriculation Centres—(contd.)

Mean marks	Sind 307.6	Deccan 300.3	Konkan 296.1	Gujarat 289.1	Karnatak 287.1
297.5		Dhulia			
297.5			Bombay		
295.0				Rajkot	
293.6			Dadar		
289.6					Dharwar
285.3					Belgaum
285.2					Bijapur
284.4				Baroda	
283.3				Ahmedabad	
282.9		Kolhapur			
268.2				Anand	

Total mean 294.8 marks.

The following table of the analysis of variance of the centres will serve as a quick test of the difference between them.

Analysis of Variance

	D.F.	S.S.	M.S.	F.
Centres	19	5090.0563	267.8977	16.51***
Groups	4	2438.0588	609.5147	37.57***
Centres within groups	15	2651.9975	176.7998	10.90***
Residual	24125	391385.5763	16.2232	s.d.=4.03
Total	24144	396475.6326		

It may be noted that the difference between groups is significantly greater than the difference between centres within a group, the ratio of their mean squares being 3.45 which is significant at 5% level for 4 by 15 degrees of freedom. The ranking of groups in the foregoing table, therefore, has a real meaning in spite of a spread of the centres.

The foregoing analysis is on the assumption that the distribution of marks furnishes a normal population. The table of the principal frequency constants, given below, will be a help to test normality.

Table of the Principal Frequency Constants

Centre or Group	No.	Mean marks	Std. error	g_1	s.d. of g_1	g_2	s.d. of g_2
Hyderabad ..	607	308.98	78.16	−.2942**	.099	.0365	.198
Karachi ..	1506	308.47	81.00	−.1519*	.063	.1491	.126
Shikarpur ..	387	302.23	83.31	−.1535	.124	.0194	.247
SIND	*2500*	*307.63*	*80.71*	*−.1859****	*.049*	*.1011*	*.098*
Sangli	379	311.03	69.60	+.3044*	.125	.4698(*)	.25
Poona ..	2549	304.28	79.65	−.1830***	.048	.3113**	.097
Sholapur ..	435	301.17	80.69	−.1723	.117	−.0066	.233
Dhulia ..	636	297.48	74.78	+.2162*	.097	.1470	.193
Kolhapur ..	745	282.93	84.55	−.2434**	.089	.0192	.178
DECCAN ..	*4744*	*300.27*	*79.57*	*−.1409****	*.035*	*.2527****	*.071*
Nasik ..	556	297.77	79.54	−.2088*	.103	.1998	.207
Bombay ..	3499	297.47	85.34	−.1802***	.041	.1950*	.083
Dadar ..	2297	293.63	79.59	−.1313**	.050	.3405***	.102
KONKAN ..	*6352*	*296.10*	*82.82*	*−.1631****	*.031*	*.2496****	*.061*
Bhavnagar ..	686	302.25	70.07	−.0425	.093	.5261**	.186
Surat ..	1553	301.57	73.80	−.0410	.062	.1322	.124
Rajkot ..	760	295.03	72.38	−.0139	.089	.0537	.177
Baroda ..	2552	284.44	77.75	−.1072*	.048	.4046***	.097
Ahmedabad ..	2077	283.35	84.87	−.0459	.054	−.0255	.107
Anand ..	433	268.24	88.54	−.0282	.117	−.1325	.234
GUJARAT ..	*8061*	*289.10*	*78.98*	*−.1010****	*.027*	*.2134****	*.054*
Dharwar ..	1035	289.57	88.37	+.0380	.076	.2928(*)	.152
Belgaum ..	979	285.27	76.52	−.0376	.078	.0071	.156
Bijapur ..	474	285.23	87.24	+.0801	.112	−.0913	.224
KARNATAK ..	*2488*	*287.05*	*83.71*	*+.0319*	*.049*	*.1779(*)*	*.098*
UNIVERSITY .	**24145**	**294.84**	**81.04**	**−.1180*****	**.016**	**.2046*****	**.031**

It may be noted that among the centres, Sangli has the greatest mean with the least variance, while Anand has the least mean with the greatest variance. High mean indicates efficiency and low variance indicates consistency : and both are desirable from the educational point of view. Sangli, therefore, leads the centres and Anand brings up the rear. It will also be seen from this table that the University as a whole is slightly but very highly significantly anormal, both in symmetry and kurtosis. The groups also show this feature but to a slightly less marked extent. The anormality of the centres is seen to be still further reduced. This, therefore, leads to the conclusion that the cause of anormality is the combination of many different groups of students in uneven numbers and with greatly varying group-standards of performance.

To trace this down to the last available source the totals of candidates appearing at the Sangli centre, one of the small centres but the best, were classified by the schools from which they appeared. Ten different schools sent more than ten candidates each. The table of frequency constants, given below, in respect of these schools and the remaining grouped together, shows that the significance of anormality disappears in most cases and that the difference in standards is quite marked. Although most of the schools individually are close to normality, all of them taken together form a significantly anormal group. This proves the contention that there is no great harm in taking the fundamental distribution of marks as normal.

Table of Frequency Constants : Sangli Centre Schools

School	No.	Mean marks	Std. error	g_1	s.d. of g_1	g_2	s.d. of g_2
C. San. @ ..	101	310.3	79.02	.1524	.24	.2197	.47
Sang. @ ..	58	318.3	71.62	.7756*	.31	.0761	.62
Mir. @ ..	38	294.1	55.58	.1360	.38	.4282	.75
San. @ ..	25	337.4	61.26	.0994	.46	−.1689	.90
P. San. ..	23	318.0	48.82	−.0213	.48	−.3394	.93
P. Jam. ..	19	324.4	49.35	.3508	.52	−2.4621*	1.01
Tas. ..	18	305.0	61.65	−.7407	.53	.1105	1.04
Ichal. ..	15	334.0	61.53	1.3462*	.58	4.7799**	1.12
Dec. ..	12	289.0	64.00	−.1912	.64	1.6199	1.23
Nimb. ..	11	329.2	78.77	.1629	.66	−.8961	1.28
Rest of Schools @	59	294.8	65.79	.5956	.31	1.2983*	.61
Sangli Centre @	379	311.0	69.60	.3044*	.125	.4698(*)	.25

@ In these cases constants are calculated by grouping ; while in the remaining cases they are calculated without grouping.
'San.' is a Girls' school.

I wish to record my thanks to Prof. D. D. Kosambi for his usual helpful guidance in my work.

FERGUSSON COLLEGE,
POONA 4

STUDIES IN EDUCATIONAL STATISTICS : VI

Ranking of High Schools by the Method of Adjusted plot Yields

By

N. R. KULKARNI,

Research Scholar, University of Bombay

THERE is a common tendency to judge a high school on the strength of the percentages of the results. But a little thinking is sufficient to show that this way of judging the schools is not satisfactory. It is very easy to score a high percentage by sending selected students for the examination. A better criterion by the method of adjusted plot yields given by R. A. Fisher in his "Statistical Methods for Research Workers" is suggested by Prof. D. D. Kosambi for ranking the educational institutions. The colleges in the Bombay University are ranked by Prof. R. P. Shintre in his "Studies in Educational Statistics," Nos. III and IV, by applying the percentage method and this method respectively. As the effect of the No. appeared is eliminated from the No. passed by the regression formula, in this method, it gives decidedly better results than that by percentage method.

By this method the high schools which are sending their students for the Matriculation examination of the Bombay University are ranked on the strength of their results in that examination. A special card* is prepared for each school and the No. passed and No. appeared for each year from 1916 to 1940 are recorded on it. These figures are taken from the University Calendars. Then the cards are sorted according to the standing of the schools.

TABLE I

Standing in years	No. of Schools	Standing in years	No. of Schools	Standing in years	No. of Schools	Standing in years	No. of Schools	Standing in years	No. of Schools
25	144	20	19	15	18	10	20	5	32
24	1	19	13	14	11	9	8	4	30
23	8	18	14	13	13	8	26	3	45
22	7	17	15	12	13	7	22	2	45
21	14	16	18	11	16	6	42	1	44

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*The University Research grant to Prof. R. P. Shintre is made use of in printing the cards, etc., as he was going to work out this problem; but afterwards the problem was handed over to me.

This table shows the rapid growth of the number of high schools in the last 10 years. There were only 144 high schools which are sending candidates for the Matriculation examination from 1916 to 1940.

Only these high schools are taken for the ranking, because their long standing for 25 years may be safely relied upon. Amongst these there are some schools which have changed their names during this period. The identity of their names is corroborated from the University authorities. If any such high school is not considered that is due to want of information only. Though only 144 high schools are taken for investigation the data of all other high schools from 1916 to 1940 are collected.

TABLE 2

Year	No. passed	No. appeared	Year	No. passed	No. appeared	Year	No. passed	No. appeared
1916	1708	3258	1925	2441	4790	1934	4063	7592
1917	1412	3683	1926	2145	4906	1935	3199	7580
1918	2115	3705	1927	2513	5433	1936	2867	8650
1919	1768	3472	1928	2353	5744	1937	1570	4184
1920	2060	3560	1929	3573	5536	1938	3931	6547
1921	1986	4015	1930	2451	6012	1939	4954	7249
1922	2446	4140	1931	4048	6616	1940	4337	7622
1923	2855	4461	1932	2929	7144	Total ..	70252	138084
1924	2816	4689	1933	3712	7496			

This table gives the total No. appeared and No. passed from all these schools (144) for different years. This together with table 1 shows that not only new schools were started, but the number in existing schools has also increased. In 1937 when the Matriculation examination was held twice in a year, the one in April according to new rules is taken into consideration. This is the reason why this year shows a sudden fall in the number of candidates appeared. In table 9 the totals of No. appeared and passed from each school in 25 years are given. In all there are 3,600 sets of paired numbers—No. appeared and No. passed. The 144×25 table is not given here for want of space. By treating the No. appeared (x) and passed (y) as preliminary and experimental plot yields in *ex.* 46.1 of Fisher's "Statistical Methods for Research Workers" the sums of squares and products are calculated. The relationship between the two variates expressed by regression of y on x, for the sets treated alike, after eliminating the differences between schools and years, is determined. After the calculation of linear regression the quadratic is tried thinking that it may suit better. Table 3 gives the sums of squares and products, and the analysis of variance of (y) No. passed after adjustment by the linear and quadratic regressions. The significance of the variances due to schools and years is tested by Fisher's *z*-test. It can be seen that the differences in schools and in years is significant at .01 percent level. Again the M. S. due to years is much larger than that due to schools, though the difference is not significant. By applying the exact test of significance given by R. A. Fisher, which makes proper allowance for the sampling errors of the co-efficients in the regression formulae, the reduced S.S. is calculated. (See table 4). By this test the M. S. due to schools is reduced by nearly half, but still it is significant at .01 percent level. There is practically no change in the M. S. due to years. Table 5 gives the analysis of residual error. If we compare the two regressions, though the error of adjusted No. is reduced slightly by the quadratic, the linear fits better because the M. S. due to quadratic is much less than that of linear. By testing the significance it is found that the two regressions do not differ significantly. It can be seen that the large part in the S. S. of unadjusted No. is due to regression. The mean square error per set is reduced nearly by half.

By pooling the schools in different ways the S.S. due to schools is broken further. Tables 6-A, B & C give the details of the classifications. Table 7 gives the sums of squares and products and adjusted S.S. by linear and quadratic regressions. In table 8-A the M. S. due to groups is compared with the M. S. due to schools within groups. It is found that the difference is not significant, *i.e.*, there is no real difference in different groups as such, but it is due to the schools within the groups. Table 8-B shows that there is a significant difference between the kinds and schools within the kinds. Similarly table 8-C shows that there is no significant difference between classes and schools within classes.

From the regression formulae the adjusted mean for each school per year is calculated and the high schools are ranked from these adjusted means. (See Table 9). It gives the ranking by three ways. The rankings by the quadratic adjustment and linear adjustment do not differ much as is to be expected from the fact that the two regressions do not differ significantly. As indicated in the beginning the high schools sending more candidates, get much weight and consequently stand higher than the smaller schools, though the percentages of the former are comparatively low. St. Xavier's, Bombay, stands first by both the methods and decidedly the best amongst all. Nutan Marathi and New English, Poona, get credit for their large numbers. The High School for Indian Girls. Poona, is 2nd by percentages but being a smaller one it stands 10th, The last 6 or 8 high schools are keeping practically the same rank by both the methods. Though Tutorial, Ahmedabad, is sending more candidates, its percentage is so low that it does not get any higher rank by adjusted method. A close observation of this list shows that the rank of a school depends both on the number of candidates sent and the percentage of the result.

I thank Professor D. D. Kosambi, Fergusson College, Poona, for his guidance.

TABLE 3

Sums of Squares and Products and Analysis of Variance of No. Passed after Adjustment

	Y	XY	X^2	YZ	XZ	Z^2	Adjusted by Linear Regression				Adjusted by Quadratic Regression			
							D.F.	S.S.	M.S.	F.	D.F.	S.S.	M.S.	F.
Schools ..	1231453	2256059	4419600	416261557	807265956	17,4188656606	143	168909.5	1181.19	24.15 ***	143	178161.9	1245.88	25.6 ***
Years ..	149360	199207	439839	26620020	58768550	7927235304	24	62278.2	2594.93	53.06 ***	24	63875.7	2661.48	54.6 ***
Residual ..	291783	336346	912294	76536693	196026436	5,9853141953	3431	167810.3	48.91	S.D. 6.99	3430	166752.5	48.62	S.D. 6.97
Total ..	1672596	2791612	5771733	519418270	1062060942	24,1969033863	3598	398998.1			3597	407890.1		

No. Passed : y

No. Appeared : x

Sq. of No. Appeared : z

$$Y^2 = \Sigma\,(y-y)^2$$

$$XZ = \Sigma(z-z)(\bar{x}-x)$$

etc. . .

Linear Regression

$$y-\bar{y} = a\ (x-x)$$

$$a = \frac{XY}{X^2}$$ from residual

Value of $a = .3686$

Quadratic Regression

$$y-\bar{y} = b\,(x-\bar{x}) + c\,(z-\bar{z})$$

Values of $b = .31699$

$c = .24\times10^{-3}$

$$b = \frac{XY.Z^2 - YZ.XZ}{Z.^2X^2 - (XZ)^2}$$

$$c = \frac{X.^2YZ - XY.XZ}{Z^2.X^2 - (XZ)^2}$$

from residual

TABLE 4

Reduced S. S. by Exact Test

	By Linear Regression				By Quadratic Regression			
	D. F.	S. S.	M. S.	F.	D. F.	S. S.	M. S.	F.
Schools	143	94980.3	664.19	13.58 ***	143	95488.1	667.74	13.73 ***
Years	24	61211.1	2550.46	52.15 ***	24	62016.7	2584.03	53.15 ***
Residual	3431	167810.3	48.91		3430	166752.5	48.62	

TABLE 5

Analysis of Residual Error

	D. F.	S. S.	M. S.
Linear Regression	1	123972.7	123972.7
Error of Adjusted No.	3431	167810.3	48.91
Error of Unadjusted No.	3432	291783	85.02
Quadratic Regression	2	125030.5	62515.2
Error of Adjusted No.	3430	166752.5	48.62
Error of Unadjusted No.	3432	291783	85.02

TABLE 6A

Schools Classified by University Groups

Groups	No. of Schools	No. Passed	No. Appeared
Deccan	30	18,489	36,165
Gujerat	52	24,220	50,564
Karnatak	11	5,124	11,061
Konkan	41	16,818	28,680
Sind	10	5,601	11,614
Total ..	144	70,252	138,084

TABLE 6B

Schools Classified by Kinds

Kind	No. of Schools	No. Passed	No. Appeared
Girls	16	3006	4867
Rest	128	67,246	13,3217
Total ..	144	70,252	138,084

TABLE 6C

Schools Classified by Management (from D. P. I.'s Report)

Class		No. of Schools	No. Passed	No. Appeared
Anglo-Vernacular Schools	Government .	18	14325	27532
Do.	Municipal ..	3	1475	3442
Do.	Aided ..	59	29048	57788
Do.	Not Aided ..	3	603	900
Anglo-Indian, European and English Teaching Schools	Aided ..	11	3985	5275
Do.	Not Aided ..	1	76	151
Native State High Schools	..	49	20740	42996
	Total ..	144	70252	138084

TABLE 7

Sums of Squares and Products and Adjusted S. S.

	Y^2	Xu	X^2	Yz	Xz	Z^2	Adjusted S. S. by Linear Regression	Adjusted S. S. by Quadratic Regression
Groups .	33004	75825	199721	15257667	35026817	7382097360	4248.59	3429.32
Kind .	64794	141415	708645	14648620	31471076	3311758434	29667.45	24193.17
Class	100116	199623	422030	16678007	37417451	4480636282	13658.74	14907.49

TABLE 8

		D F.	By Linear Regression			By Quadratic Regression		
			S. S.	M. S.	F.	S S.	M. S.	F.
8 A	Groups	4	4248.59	1062.15	1 11	3429.32	857.33	1.46
	School within Groups	139	164660.95	1184.61		174732.61	1257.07	
8-B	Kind	1	29667.45	29667.45	30.25 ***	24193.2	24193.2	22.31 ***
	Schools within kind	112	139242.09	980 54		153968.73	1084.29	
8 C	Class	6	13658.74	2276.46	2.01	14907.49	2484.58	2.01
	Schools within class	137	155250.8	1133.22		163254.44	1191.64	

TABLE 9

Name and Place	No. Passed	No. Appeared	By Quadratic Regression		By Linear Regression		By Percentage	
			Mean No. Adjusted by Quadratic Regression	Rank	Mean No. Adjusted by Linear Regression	Rank	Total Percentage	Rank
1	2	3	4	5	6	7	8	9
St. Xavier's, Bombay..	1589	1860	51.429	1	50.274	2	85.43	1
Nutan Marathi Vidyalaya, Poona	2813	5130	49.337	2	51.022	1	54.83	49
New English, Poona ..	3045	5837	46.973	3	49.878	3	52.17	61
Baroda, Baroda ..	2158	3877	43.469	4	43.296	4	55.66	45
Elphinstone, Bombay,..	1613	2614	42.524	5	40.117	5	61.71	26
Wilson, Bombay ..	1128	1478	38.419	6	37.467	6	76.32	7
T. & T. V. Sarvajanik, Surat	1269	2050	35.589	7	34.673	7	61.90	25
Ranchhodlal Chhotalal, Ahmedabad	1179	2067	32.138	8	30.822	8	57.04	41
N. J. V., Karachi ..	1305	2471	31.178	9	29.906	10	52.81	57
High School for Indian Girls, Poona	729	855	30.860	10	30.692	9	85.26	2
Ahmednagar Society's, Ahmednagar	1042	1791	30.320	11	29.412	11	58.18	33
Nasik, Nasik ..	973	1726	28.506	12	27.610	12	56.37	42
Shri Sayaji, Baroda ..	875	1556	27.072	13	26.197	13	56.23	43
Nawanagar, Jamnagar	732	1211	26.146	14	25.559	14	60.45	31
Sir C. J. N. Z. Madressa, Navsari	817	1500	25.620	15	24.702	17	54.47	50
Navalrai Hiranand Academy, Hyderabad ..	1197	2562	25.498	16	24.234	19	46.72	94
Ratnagiri, Ratnagiri ..	679	1108	25.492	17	24.962	15	61.28	29
B. J., Thana ..	730	1263	25.397	18	24.715	16	57.80	37
D. E. Society's New English, Satara	991	1998	25.263	19	24.319	18	49.60	77
Sangli, Sangli ..	792	1478	24.945	20	24.027	20	53.59	54
Rajaram, Kolhapur ..	1054	234	24.573	21	23.360	22	47.18	91
Garud, Dhulia ..	740	1421	23.677	22	22.787	25	52.08	63
St. Patrick's, Karachi	464	608	23.569	23	23.734	21	76.32	8
Alfred, Rajkot ..	1449	3332	23.524	24	22.971	24	43.49	111
Government, Nadiad ..	680	1263	23.431	25	22.717	26	53.84	52

TABLE 9—(*contd.*)

Name and Place	No. Passed	No. Appeared	By Quadratic Regression: Mean No. Adjusted by Quadratic Regression	By Quadratic Regression: Rank	By Linear Regression: Mean No. Adjusted by Linear Regression	By Linear Regression: Rank	By Percentage: Total Percentage	By Percentage: Rank
1	2	3	4	5	6	7	8	9
King George, Dadar ..	603	1035	23.272	26	22.998	23	58.26	32
Bahadur Khanji, Junagadh ..	718	1419	22.707	27	21.937	30	50.60	70
Esplanade, Bombay	565	977	22.702	28	22.333	29	57.83	35
Aryan Education Society's, Bombay	747	1534	22.381	29	21.401	34	48.70	82
R. S. Dalal, Broach ..	714	1439	22.361	30	21.482	33	49.62	76
Dravid, Vai ..	449	656	22.340	31	22.426	28	68.45	16
Private, Rajapur ..	425	585	22.327	32	22.513	27	72.65	11
Alfred, Bhavnagar ..	956	2118	22.319	33	21.150	40	45.14	102
Sardar's, Belgaum ..	748	1544	22.308	34	21.293	35	48.45	84
Bai Avabai, Bulsar ..	647	1247	22.258	35	21.632	31	51.88	65
Chubildas Lulloobhoy Boys', Dadar	724	1460	22.186	36	21.572	32	49.59	78
Dharwar, Dharwar ..	835	1803	22.036	37	20.955	42	46.31	96
Goverdhandas, Jalgaon	712	1463	21.946	38	21.048	41	48.67	83
Anant Shivaji Desai, Malwan	577	1086	21.624	39	21.206	38	53.13	55
Gokuldas Tejpal, Bombay	521	937	21.371	40	21.163	39	55.60	46
Parshurambhau, Jamkhind	453	748	21.295	41	21.230	37	60.56	30
Satara, Satara ..	647	1344	20.929	42	20.202	45	48.14	86
Karwar, Karwar ..	653	1364	20.198	43	20.147	46	47.87	89
St. Vincent's, Poona ..	350	466	20.903	44	21.268	36	75.11	9
St. Paul's, Belgaum ..	304	398	19.938	45	20.430	43	76.38	6
Babu Panalal P. Jain, Bombay	287	354	19.82	46	20.399	44	81.07	3
Sir Jaswatsinhji, Limbdi	392	679	19.763	47	19.807	49	57.73	38
Shikarpur, Shikarpur	539	1132	19.536	48	19.008	53	47.61	90
Telang, Godhra ..	430	814	19.500	49	19.337	51	52.83	56
Sagramji, Gondal ..	314	466	19.438	50	19.828	48	67.38	17

TABLE 9—(*contd.*)

Name and Place	No. Passed	No. Appeared	By Quadratic Regression		By Linear Regression		By Percentage	
			Mean No. Adjusted by Quadratic Regression	Rank	Mean No. Adjusted by Linear Regression	Rank	Total Percentage	Rank
1	2	3	4	5	6	7	8	9
Sind Madressah-tul-Islam, Karachi	582	1266	19.393	51	18.752	54	45.97	98
St. Mary's, Bombay ..	295	413	19.387	52	19.849	47	71.43	12
St. Columba, Bombay	339	550	19.290	53	19.589	50	61.64	27
Victoria Jubilee, Pandharpur	501	1042	19.165	54	18.666	55	48.08	87
Patan, Patan ..	591	1319	19.066	55	18.331	60	44.81	103
Amreli, Amreli ..	457	936	18.928	56	18.618	56	48.82	81
M. E. Society's, Poona	902	2195	18.804	57	17.855	65	41.09	123
Northcote, Sholapur ..	561	1258	18.701	58	18.030	63	44.59	104
Antonio Da Silva, Dadar	288	446	18.666	59	19.082	52	64.57	19
Municipal, Sukkur ..	640	1526	18.116	60	17.239	78	41.94	118
Cambay, Cambay .	353	688	18.060	16	181.14	62	51.31	67
St. Andrew's, Bandra	265	422	18.052	62	18 516	57	62.80	23
Beynon Smith, Belgaum	712	1723	17.967	63	17.214	79	41.32	120
Sardar Dastur Hoshang Boys', Poona	252	394	17.917	64	18.409	58	63.96	21
Sir Ajitsinhaji, Dhrangadhra	342	679	17.759	65	17.807	67	50.37	72
Alfred, Bhuj ..	339	673	17.705	66	17.776	69	50.37	71
Gokulbhai D, Visnagar	325	639	17.596	67	17.717	71	50.86	68
Alexander Girls' Eng. Institution, Bombay	195	244	17.568	68	18.341	59	79.92	4
Sir J. J. Parsi Benevolent Inst., Bombay	222	330	17.549	69	18.153	61	67.27	18
St. Joseph's Convent, Bandra	205	293	17.336	70	18.019	64	69.97	13
Palanpur, Palanpur	361	769	17.285	71	17.240	77	46.94	92
Bijapur, Bijapur ..	587	1438	17.276	72	16.416	94	40.82	126
Gibb., Kunta ..	275	521	17.176	73	17.457	74	52.78	58
Bhavsinhji, Porbander	270	512	17.069	74	17.389	75	52.73	59
S. S., Aundh ..	236	412	17.038	75	17.504	72	57.28	40

TABLE 9—(*contd.*)

Name and Place	No. Passed	No. Appeared	By Quadratic Regression		By Linear Regression		By Percentage	
			Mean No. Adjusted by Quadratic Regression	Rank	Mean No. Adjusted by Linear Regression	Rank	Total Percentage	Rank
1	2	3	4	5	6	7	8	9
Sheth Gokuldas Tejpal, Cutch-Mandvi	174	222	17.023	76	17.825	66	78.38	5
Chanda Ramaji Hindu Girls', Bombay	180	241	17.018	77	17.785	68	74.69	10
Jubilee Institution, Umreth	352	762	17.017	78	16.983	83	46.19	97
Sanatan Dharma, Bhavnagar	499	1202	16.991	79	16.374	96	41.51	119
Alfred Gidney, Dapoli	229	396	16.966	80	17.460	73	57.83	36
Naranbhai Keshavlal, Petland	558	1381	16.941	81	16.098	101	40.41	130
Vakhtuba Charitable, Morvi	244	443	16.930	82	17.367	76	55.08	47
Miraj, Miraj ..	273	543	16.802	83	17.052	81	50.28	74
Seth M. & R. Tata, Bilimoria	224	401	16.698	84	17.186	80	55.86	44
Daji Raj, Wadhwan ..	351	800	16.524	85	16.383	95	43.88	107
Shikarpur Academy, .. Shikarpur	351	803	16.438	86	16.339	97	43.71	109
Sir Siddi Ahmedkhan, Murud-Janjira	256	519	16.434	87	16.726	87	49.33	79
Wankaner, Wankaner	195	336	16.385	88	16.984	82	58.04	34
School of the Sacred H. of Jesus, Bardez	214	396	16.362	89	16.860	85	54.04	51
Robert Money, Bombay	345	794	16.320	90	16.232	99	43.45	112
New English, Nadiad	433	1054	16.297	19	15.918	104	41.08	124
Maharani, Baroda ..	254	517	16.295	92	16.676	88	49.22	80
Jamshedji N. Petit .. Parsi Orphanage, Bombay	175	284	16.265	93	16.952	84	61.62	28
Tulsibhai Bakorbhai, Bhadran	227	448	16.214	94	16.613	89	50.67	69
Anjuman-i-Islam, Bombay ..	205	395	16.004	95	16.513	92	51.90	64
Parsi, Panchgani	158	252	15.998	96	16.743	86	62.70	24
St. Joseph's, Arpora, Bardez	198	377	15.966	97	16.500	93	52.52	60
Savantwadi, Savantwadi	280	639	15.948	98	15.917	105	43.82	108
Zoroastrian Boarding, Deolali ..	167	291	15.854	99	16.528	91	57.39	39
John Elphinstone, Alibag	274	618	15.837	100	15.986	103	44.34	106

TABLE 9—(*contd.*)

Name and Place	No. Passed	No. Appeared	By Quadratic Regression		By Linear Regression		By Percentage	
			Mean No. Adjusted by Quadratic Regression	Rank	Mean No. Adjusted by Linear Regression	Rank	Total Percentage age	Rank
1	2	3	4	5	6	7	8	9
Young Ladies, Bombay	147	232	15.814	101	16.598	90	63.36	22
Bhor, Bhor ..	201	400	15.793	102	17.767	70	50.25	75
Fort and Propriety, Bombay ..	357	880	15.695	103	15.443	112	40.57	128
Private, Pen ..	164	298	15.633	104	16.305	98	55.03	48
Maharani Chimanabai, Baroda	401	1019	15.500	105	15.154	121	39.35	132
Basel Mission, Dharwar	264	623	15.356	106	15.513	111	42.38	114
Sirdar Dastur N. Girls', Poona	119	185	15.298	107	16.171	100	64.32	20
A. P. Mission, Vengurla	180	375	15.282	108	15.809	107	48.00	88
M. K. Natha Bhatia; Bombay	141	262	15.183	109	15.915	106	53.82	53
Mudhoji, Phaltan ..	194	425	15.167	110	15.632	109	45.65	99
Motibhai Mathurbhai, Sojitra	264	642	15 141	111	15.233	177	41.12	122
I P. Mission, Surat ..	233	551	15 092	112	15.334	114	42.29	115
Queen Mary, Bombay	99	143	15.037	113	15.989	102	69.23	14
Union, Surat ..	401	1059	15.007	114	15.564	132	37.87	135
Harris, Palitana ..	168	395	14.996	115	15.565	110	46.80	93
Private, Kolhapur	456	1227	14.932	116	14.287	135	37.16	136
Lamington, Hubli .	334	874	14.853	117	14.612	131	38.22	134
V. N., Dharmaj ..	190	442	14.803	118	15.221	118	42.99	113
St. Helena's, Poona	88	128	14.788	119	15.771	108	68.75	15
Kundamal Girls', Hyderabad ..	236	578	14.781	120	15.056	123	40.83	125
Sir C. J. Readymoney, Gandevi	137	284	14.742	121	15.431	113	48.24	85
Sir D. M. Petit, Sangamner ..	230	568	14.740	122	14.967	125	40.49	129
Church Mission Society, Karachi	165	372	14.718	123	15.253	116	44.35	105
American Mission, Ahmednagar ..	165	379	14.624	124	15.150	122	43.54	110
N. M. Wadia, Nargol ..	140	308	14.546	125	15.197	119	45.45	101

TABLE 9—(*concld.*)

Name and Place	No. Passed	No. Appeared	By Quadratic Regression		By Linear Regression		By Percentage	
			Mean No. Adjusted by Quadratic Regression	Rank	Mean No. Adjusted by Linear Regression	Rank	Total Percentage	Rank
1	2	3	4	5	6	7	8	9
Edward Memorial, Kaira	196	482	14.517	126	14.872	127	40.66	127
Shri Mohandavji, Dharampur	136	299	14.510	127	15.170	120	45.48	100
American Mission for .. Girls, Ahmednagar	97	186	14.402	128	15.276	115	52.15	62
L. S., Sidhpur ..	162	405	14.230	129	14.647	129	40.00	131
Jivakore Lallubhai, . Ahmedabad	287	784	14.160	130	14.059	137	36.61	137
Maratha, Bombay ..	321	898	14.087	131	13.738	139	35.75	138
Bai Ruttonbai F. D. Panday Girls', Bombay	74	143	14.035	132	14.990	124	51.75	66
Sir Jacob Sassoon Jewish, Byculla	75	151	14.012	133	14.952	126	50.33	73
Nava Kanya Vidyalaya, Hyderabad	122	296	13.963	134	14.654	128	41.22	121
I. P. Mission Girls', .. Surat	61	131	13.663	135	14.647	130	46.56	95
Coronation, Mangrol	74	175	13.625	136	14.518	133	42.29	116
Bai Motlabai Wadia Girls', Broach	61	145	13.490	137	14.440	134	42.07	117
Cathedral and John Conon, Bombay ..	38	98	13.172	138	14.213	136	38.78	133
Radhanpur, Radhanpur	64	184	13.111	139	13.985	138	34.78	139
S. P. G. Mission, Ahmednagar	41	177	12.276	140	13.169	140	23.16	143
Tutorial, Ahmedabad	1135	3270	11.963	141	11.325	141	34.71	140
Saurashtra, Rajkot ..	164	693	10.452	142	10.481	142	23.67	142
Union, Broach ..	207	821	10.446	143	10.313	143	25.21	141
City, Kolhapur ..	198	973	7.969	144	7.716	144	20.35	144

OPTICAL METHOD OF MEASURING THE ANGLE OF CONTACT

By

S. J. Khambata and A. B. Sahiar

THE importance of the angle of contact in problems of surface tension prompted the authors to measure the same optically. By forming interference fringes in the film, an exact measurement of the size and the shape of the liquid at the edge of contact is obtained. Turpentine and water are examined by this method and it is found that the angle of contact of air—turpentine—glass is nearly 0.4 degree at 28°.6C., whereas the accepted value is 17 degrees (Kaye & Laby—Physical Constants). For water, when the glass is very carefully cleaned, the results establish the fact that the angle of contact of air—water—glass is zero.

The method of measurement is essentially the same as for interference fringes formed by reflected light. Visual observations were made on many films in order to study the behaviour of the fringes, but it was not possible to take the readings directly. All the readings recorded are from the photographs.

The liquid under observation is taken in a glass cell, and an optical flat, a black mirror from the interferometer, is clamped vertically in it. The black mirror is essential to obtain bright fringes. It is difficult to observe them with clear glass flats on account of the back reflection. The liquid is poured in the cell carefully, till it stands heaped over the edge of the cell as shown in Fig. 1.

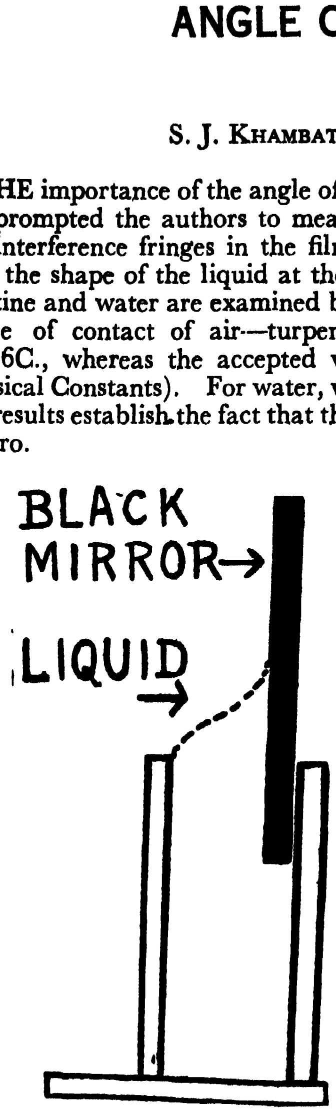

Fig. 1

A parallel beam of light from a sodium vapour lamp is reflected from a piece of mirror glass, which has a small portion from its centre scratched clear, on to the liquid surface. The returning beam of light passes through the clear glass and is observed. With high or medium power objectives it is found convenient to attach the mirror on the objective of the microscope. A hole is bored in a piece of cork to slip it on the objective. The face of the cork is cut at an angle of 45 degrees, and the tiny piece of mirror is fixed on to it with some soft wax. With this arrangement and a 45 watts sodium vapour lamp the exposures are conveniently short. Two or three seconds are ample on Ilford rapid process Panchromatic plates. In order to prevent the surface of the film from being disturbed, the glass cell is covered with a box, having a hole in the front. The space in the box is kept saturated by leaving a large pool of the liquid at the bottom.

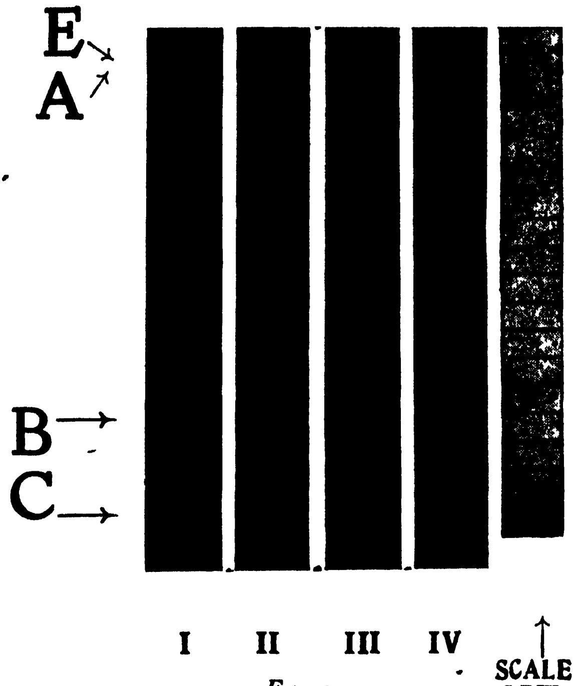

Fig. 2

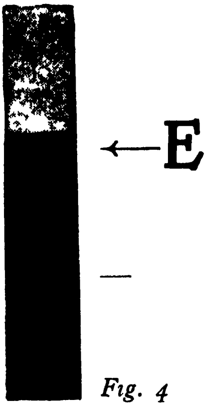

Fig. 4

Figure 2 shows the appearance of the fringes with turpentine (Merck's rectified). At E the edge of contact, 4 fine white fringes are seen. From B to C, 5 to 7 more fringes appear. Once the steady stage is reached, which requires about ten to fifteen minutes after pouring the liquid on the optical flat, the fringes at E and between B and C remain constant.

Between A and B the surface exhibits periodic *storms*. Figures 2 (i) to (iv) show these changes. The general appearance of the fringes in the steady state is very like Fig. 2 (iii). Three broad white fringes appear between A and B. No such change is noted at E or between B and C.

TURPENTINE

(*Merck's rectified*)

Temperature of the liquid 28°.6C. Mean $\lambda=5893\times10^{-8}$ cm.

No. of the white band	Average dist. of the band from the edge E in cms.	Average dist. of the band from the edge E in units of wave length	
Top edge E (black band)	0	0	
1	0.002037	34.57	E to A
2	0.004340	73.66	
3	0.006422	109.05	
4	0.008724	148.05	
5	0.1379	2340.5	B to C
6	0.1440	2444.5	
7	0.1502	2549.0	
8	0.1561	2649.0	
9	0.1597	2710.5	
10	0.1620	2749.5	

As the thickness of the film varies from a dark band to the neighbouring bright band by $\lambda/4$

$$\text{Tan } a=\frac{0.25}{34\cdot57}$$

$$a= 0.4 \text{ of a degree.}$$

Between E and A, the equation of the curve is approximately
$y=a+151x-51.04x^2$

From this equation, $a=0.37$ of a degree.

$\therefore$ The angle of contact of turpentine is nearly 0.4 degree.

A graph is drawn on a large scale showing the distances of the fringes and the thickness of the film, both scales being in units of λ.

The angle of contact from this graph is 0.4 degree.

Figure 3 shows the shape of the film. It is not drawn to scale.

It is interesting to note that the tangent will make an angle of seventeen degrees with the Y axis at some point on the curve below C (Fig. 3). Fine fringes can be seen in this region directly with an eye-piece. With the magnification used, these fringes could not be photographed. This fact shows that the previous workers observed the angle of contact at some point below C and did not observe or take into consideration the fine film clinging to the glass plate above the point C.

WATER

Figure 4 shows the film of water on clean glass. The glass flat was kept in dilute chromic acid over-night and washed very carefully with several changes of distilled water. There are no interference bands at the edge of contact as with turpentine. The first broad band 0.3 mm. wide of grey colour shows that the film is uniform in thickness and the angle of contact is zero.

If the glass flat is washed with soap and water, it is noted that at the edge of contact fine bands of the turpentine type appear. In this case the edge is not straight and the bands are not parallel, and the spacings between the bands at different points on the same plate are different.

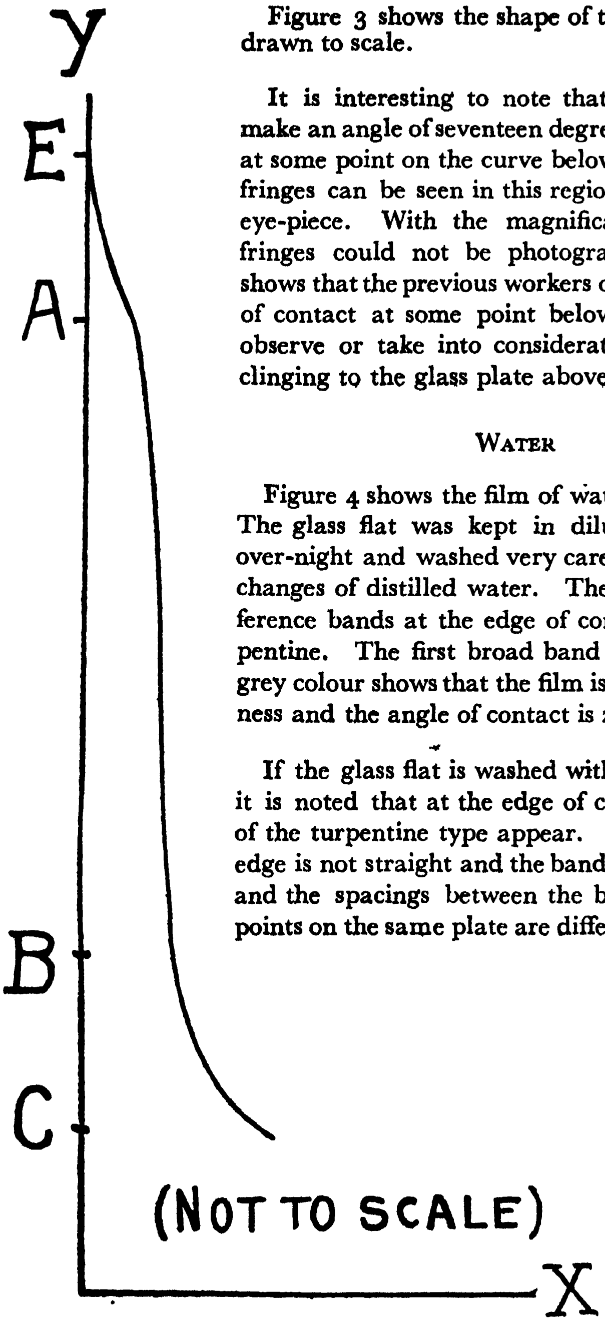

Fig. 3

ST. XAVIER'S COLLEGE,
BOMBAY

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DIPOLE MOMENT AND MOLECULAR STRUCTURE

Part V—Dipole Moments of Derivatives of Ethylene Glycol and of Glycerides

By

S. D. GOKHALE, N. L. PHALNIKAR AND S. D. BHAWE

DIELECTRIC properties of Glycerides have already been reported (Bhide and Bhide, J. Uni. Bombay, Vol. VIII, Part 3, p. 220, 1939). In this paper the dipole moments of some Glycerides and the closely related Glycol derivatives have been reported.

EXPERIMENTAL

Materials :—Monomyristin and Monostearin were prepared by the method of Malkin and Shurbagy (J. C. S., 1936, 1628). Ethylene glycol monomethyl ether and the corresponding ethyl ether and acetate were purchased from Dr. Schuchardt. The rest of the derivatives were prepared in the laboratory by standard methods. All the substances were carefully purified before use.

The apparatus :—This was essentially the same as the one used in previous papers of this series. The high tension unit used was, however, of a new type. This consisted of a halfwave rectifier circuit using an indirectly heated diode, followed by two stages of choke and capacity ripple filter.

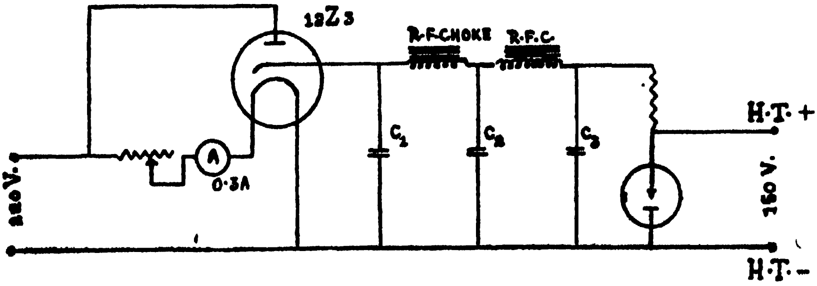


Fig. 1—The High Tension Unit

C_1, C_2 are 16 μFD Electrolytic condensers—450 V.

C_3 is a 8 ,, ,, ,, ,,

Because of the indirectly heated rectifier tube, the A. C. line voltage fluctuations have little effect on the output of the rectifier, once it has reached the thermal saturation stage. As an additional precaution, at the output of the power supply a 220 V. Neon tube with the base resistance removed was used in series with a fixed resistance as a voltage stabiliser. The voltage across the Neon tube—about 150 V.—was taken as the source of H. T. for the oscillator. It was found that this simple arrangement enabled a regulation of H. T. supply voltage comparable to that obtained by more elaborate circuits.

All the measurements were carried out at 30° C., with the exception of those of monomyristin and monostearin. The moments of these substances were determined at 50° C. The method of calculation of moments was the same as given in earlier papers.

Tables I-A and I-B give the physical constants of the substances used.

TABLE I-A

Substance	Present Work B.P.	Pressure mm.	B.P.	Pressure mm.
Ethylene glycol monomethyl ether ..	125	710	124.9	767
,, ,, monoethyl ether ..	134	,,	134.8	743
,, ,, monoacetate ..	184—85	,,	187—9	
,, ,, diacetate ..	180—81	,,	186—7	
Methoxy ethanol acetate	140	,,	145	762
Ethoxy ethanol acetate	156—58	,,		
Methoxy ethanol myristate	220	35		
Diethyl succinate	215	710	217.7	
	M.P.		M.P.	
Methoxy ethanol stearate	28.5—29			
Ethoxy ethanol stearate	33.5			
Ethylene glycol dimyristate	63			
Ethylene glycol distearate	79.5		79	(76)
Monomyristin	70.5		70.5*	
Monostearin	80.5		80.5*	

* Malkin and Shurbagy (*loc. cit.*).

The boiling points given in the last column are taken from the Dictionary of Organic ompounds by Heilbron.

TABLE I-B

Substance	Density at 30° C.	Refractive Index at 30° C.
Ethylene glycol monomethyl ether ..	0.9532	1.3978
„ „ monoethyl ether ..	0.9254	1.40321
„ „ mono acetate ..	1.0967	1.41633
„ „ di acetate ..	1.0922	1.41176
Methoxy ethanol acetate	0.9914	1.39604
Ethoxy ethanol acetate	0.9743	1.40032
Diethyl succinate	1,0285	1.41524

Tables II and III give the data necessary for the calculation of dipole moments.

The dipole moments have been calculated in Debye units.

The solvent used was Benzene which had the following properties :—

i	Density	at 30° C.	.8670 gm/cc
ii	Dielectric constant	„	:—2.2625
iii	Refractive index	„	:—1.49274

TABLE II

Substance	α	α'	β
Ethylene glycol monomethyl ether ..	2 7956		0.0651
„ „ monoethyl ether ..	2.8150		0.0392
„ „ mono acetate ..	3.1648		0.2570
„ „ di acetate	3.0725		0.3719
Methoxy ethanol acetate	2.5856		0.1792
Ethoxy ethanol acetate	2.8236		0.1771
Methoxy ethanol myristate .. .	2.3365	−0.1962	0.0782
Methoxy ethanol stearate	2.0914	−0.2930	0.0425
Ethoxy ethanol stearate	2.3837	−0.2430	0.0613
Ethylene glycol di myristate	2.6460	−0.4826	0.1775
„ „ di stearate	2.4435	−0,5588	0.7628
Mono stearin	3.3855		0.5233
Mono myristin	3.5102		0.5075
Diethyl succinate	3.1925		0.3812

TABLE III

Substance	P_1^∞	P_E	μ
Ethylene glycol monomethyl ether	118.01	19.23	2.20
„ „ monoethyl ether	124.13	23.74	2.22
„ „ mono acetate	134.85	23.81	2.34
„ „ di acetate	143.02	33.24	2.32
Methoxy ethanol acetate	120.05	28.54	2.13
Ethoxy ethanol acetate	135.36	33.02	2.25
Methoxy ethanol myristate	174.14	87.18	2.08
Methoxy ethanol stearate	185.98	103.61	2.02
Ethoxy ethanol stearate	201.10	109.43	2.13
Ethylene glycol di myristate	248.83	142.55	2.30
„ „ di stearate	282.95	178.69	2.26
Mono stearin	225.32	50.66	3.04
Mono myristin	210.19	41.42	2.99
Diethyl succinate	156.57	40.40	2.38

DISCUSSION OF RESULTS

In the earlier stages of the work on dipole moments the measurements were interpreted on the basis of individual bond moments and the angle between them by the vector addition of the moments; but recently evidence has been forthcoming for hindered rotation even in the case of simple compounds like Ethane (Howard, J. Chem. Phys., 5, 451, 1937). Hence the results have been discussed below only in a qualitative manner. Table IV summarises the effect of substitution of a hydrogen atom in an OH group in glycol by an ethyl or a methyl group.

TABLE IV

Substance	μ	Substance	μ
Ethylene glycol	2.30	Ethylene glycol mono acetate	2.33
Methoxy ethanol	2.20 (2.04)	Methoxy ethanol acetate	2.13
Ethoxy ethanol	2.22 (2.08)	Ethoxy ethanol acetate	2.25

Byers (J. Chem. Phys., 7, 175, 1939) has determined the dipole moments of a series of Glycol derivatives known by the trade name Cellusolves. The values given in brackets are those found by Byers.

The values obtained by Byers are somewhat lower than those in the present paper. The Cellusolves used were commercial samples and Byers has not mentioned their boiling points. Probably they were not purified before use and the differences in the values obtained by him and those obtained by us may be due to the impurities in the samples Byers used. The substances we used were carefully purified by distillation and showed steady boiling points.

The results indicate that the replacement of a Hydrogen atom of the OH group by a methyl group lowers the moments. The ethyl group has a similar effect, only to a smaller degree. In the case of Ethylene glycol acetates the methyl or the ethyl group gives a similar result. The reduction in the moment due to the introduction of the ethyl or the methyl groups has been ascribed by Byers to the repulsion between the methyl group and the hydrogen of the second hydroxyl group. The reduction of the moment of the acetates is also likely to be due to a similar repulsion.

TABLE V

Ester	Moment
Ethylene glycol di acetate	2.320
„ „ di myristate	2.297
„ „ di stearate	2.260

It appears that an increase in the length of the chain in the carboxylic acid has little effect on the dipole moment. Previous results on methyl esters of fatty acids and diethyl esters of straight chain dicarboxylic acids show a similar behaviour as can be seen from the following table.

TABLE VI

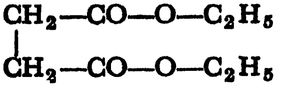
Ester	Moment	Ester	Moment
Methyl acetate	1.78	Diethyl oxalate	2.52
„ propionate	1.74	„ malonate	2.57
„ butyrate	1.77	„ succinate	2.14 (Soln.)
„ valerate	1.68	„ succinate	2.28—2.32 (Gas)
„ myristate	1.74	„ glutarate	2.42
		„ adipate	2.42
		„ sebacate	2.50

The values of moments given above are taken from the table of moments given in Trans. Far. Society, 1934.

With the exception of diethyl succinate the moments appear to be the same for one series of esters, as observed in the case of both the series, howsoever long the length of the carbon chain of the carboxylic acid be. The low value—2.14—for diethyl succinate (Solution method) is attributed by Smyth and Walls (J. Am. C.S., *53*, 527, 1931) to the carboxylic groups in the succinate being close to one another. Evidence other than dipole moments has been given by these authors, such as the ease of formation of anhydride, its viscosity, etc., in favour of this argument.

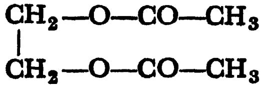
In the case of diesters of glycol the structure is similar to that of the succinate, in that the distance between the ester groups is the usual distance between the two carbon atoms in an aliphatic chain.

Diethyl succinate



$$\begin{array}{l} CH_2-CO-O-C_2H_5 \\ | \\ CH_2-CO-O-C_2H_5 \end{array}$$

Ethylene glycol di acetate



$$\begin{array}{l} CH_2-O-CO-CH_3 \\ | \\ CH_2-O-CO-CH_3 \end{array}$$

The moments of the diesters are about 2.26 to 2.32, i.e. nearly of the same order as that of diethyl succinate—2.28 to 2.32 (gas) and probably their structures are similar.

The value of the moment of diethyl succinate, *viz.*, 2.14 at 25° C., given by Smyth and Walls is incorrect. The concentrations they used were rather too high—the molfractions ranging from 0.03 to 0.15. The values of dielectric constants given in their data were plotted against the molfractions and the graph showed a distinct curvature.

We worked with much more dilute solutions in Benzene the molfractions ranging from 0.009 to 0 039. The graphs of dielectric constants and densities against the corresponding molfractions were observed to be straight lines. The value of the moment we obtained by using Hedestrand's method of calculation is 2.38. This agrees better with the value in the vapour condition.

It is also interesting to compare the moments of glycerides.

TABLE VII

Compound	Moment
Trilaurin	2.59
Tristearin	2.70
Monomyristin	2.99
Monostearin	3.04

It has been shown that the triglycerides have two structures (Clarkson and Malkin, J. C. S., 1934, 666) one of them being tuning fork like and the other a tilted chain. If the triglyceride has a tuning fork like structure and the carbon chains in one plane, the resultant moment of the triglyceride should be equal to that of methyl stearate or methyl myristate (1.74). The observed moment of tristearin—2.7 (Stoops, J. Phys. Chem., *35*, 1704, 1931) and trilaurin—2.59 (Deshapande and Paranjpe, J. Uni. Bom., Vol. IX, Part 3, p. 24, 1940) are much greater than this value and also greater than that of Ethylene glycol di-myristate. Therefore, in solution, one of the acid chains must be making an angle with the other two acid chains.

It appears surprising at first sight that the moment of tristearin should be less than that of monostearin. This lower value can be accounted for in the following way. The total moment of the triglyceride may be supposed to be composed of those of the ester groups and if the dipole moments were in the same direction the value of the total moment should have been $3 \times 1.84 = 4.52$. If one of the ester groups pointed in a sense opposite to that of the other two ester groups, as has been shown to be the case by Malkin, one should expect the value of the moment of the triglyceride to be about 1.84, while it is actually 2.7. The high value for the monoglyceride must be due to the easy rotation of the corresponding hydroxy groups in the glyceride.

TABLE VIII

Compound	Moment
Methoxy ethanol acetate	2.13
Ethoxy ethanol acetate	2.25
Methoxy ethanol myristate	2.08
Methoxy ethanol stearate	2.02
Ethoxy ethanol stearate	2.13
Ethylene glycol di acetate	2.32
,, ,, di myristate	2.30
,, ,, di stearate	2.26

It can be seen from table VIII that the differences in the moments of acetates and stearates are small and therefore the structures of the compounds must be analogous. In the case of stearates and myristates, rotation round the C—C axis of the glycol should be difficult at 30° and since the moment is not much different from that of the acetates, this shows that even in the diacetate the rotation is considerably hindered.

We are thankful to Prof. B. V. Bhide, Head of the Chemistry Department, for the interest he took during the progress of the work. Our thanks are also due to Mr. R. P. Thatte for kindly designing the H. T. unit.

MAHARAJA PRATAPSINHA
CHEMICAL LABORATORY,
SIR PARASHURAMBHAU COLLEGE,
POONA

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STUDIES IN HYDROLYSIS

By

B. E. MIRZA AND G. D. ADVANI

II—Comparison of the Saponification Constants of the Phenyl Esters of Fatty Acids with those of the corresponding completely reduced Compounds namely the Cyclohexyl Esters of the same Fatty Acids

THE object of this investigation has been to determine the saponification constants of the Phenyl and the Cyclohexyl esters of the fatty acids and the relation existing between the saponification constants of the above saturated and the completely reduced compounds and between the esters of one alcohol with the homologous acids. (*Vide* paper by the authors, J. U. B. *X*,*3*, 72, 1941).

EXPERIMENTAL

The 93 per cent neutral Ethyl Alcohol, which was used as solvent, and Alcoholic Potassium Hydroxide were prepared in the same way as described in our previous paper. (*Ibid.* 72, Nov. 1941).

Esters :—All the Cyclohexyl esters and Phenyl Acetate were supplied by "Poulène Frères, France." They were again purified by distillation before use.

Phenyl Propionate and Phenyl Butyrate were prepared by the authors in the Laboratory according to the directions given in Beilstein's Dictionary and were purified until they had the correct boiling points.

The procedure adopted in the saponification of the esters and the calculation of the velocity constants were done in the same way as described in our previous paper. (*Ibid.* 73, Nov. 1941).

RESULTS AND DISCUSSION

In Table I below are given the saponification constants of all the esters saponified by 0.1001 Potassium Hydroxide.

TABLE I

Name of Ester	Mean Saponification Constant
Phenyl Acetate	0.000155524
Phenyl Propionate	0.0000672333
Phenyl Butyrate	0.00003256
Cyclohexyl Acetate	0.00464220
Cyclohexyl Propionate	0.00188637
Cyclohexyl Butyrate	0.000884064
Cyclohexyl Iso-Butyrate	0.000215624

Values of the constants in duplicate experiments did not differ more than 0.3%.

The velocity of saponification of the Phenyl esters of the fatty acids is, in all cases, less than that of the corresponding Cyclohexyl esters of the same fatty acids. This is as it should be, just as in the case of Cresyl and Methyl-Cyclohexyl esters. (*Ibid.* 75, Nov. 1941).

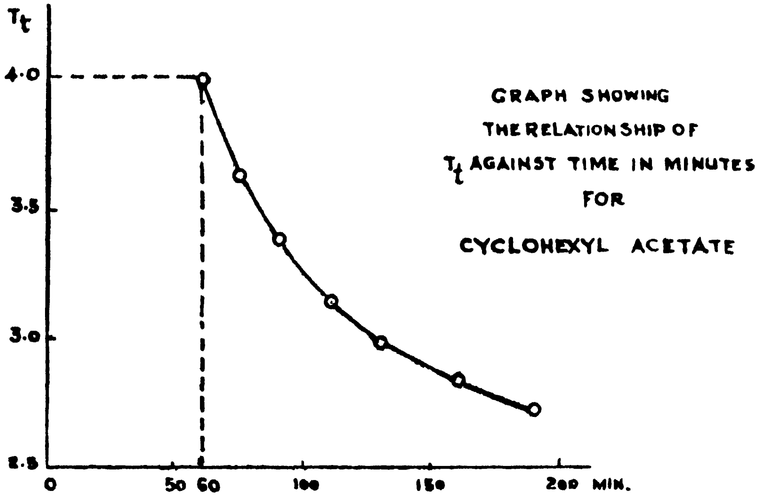
TABLE II

Names of Esters	Saponification Constants	Ratio
$\frac{\text{Cyclohexyl Acetate}}{\text{Phenyl Acetate}}$	$\frac{0.004642}{0.0001555}$	29.85
$\frac{\text{Cyclohexyl Propionate}}{\text{Phenyl Propionate}}$	$\frac{0.001886}{0.00006723}$	28.05
$\frac{\text{Cyclohexyl Butyrate}}{\text{Phenyl Butyrate}}$	$\frac{0.0008841}{0.00003256}$	27.15

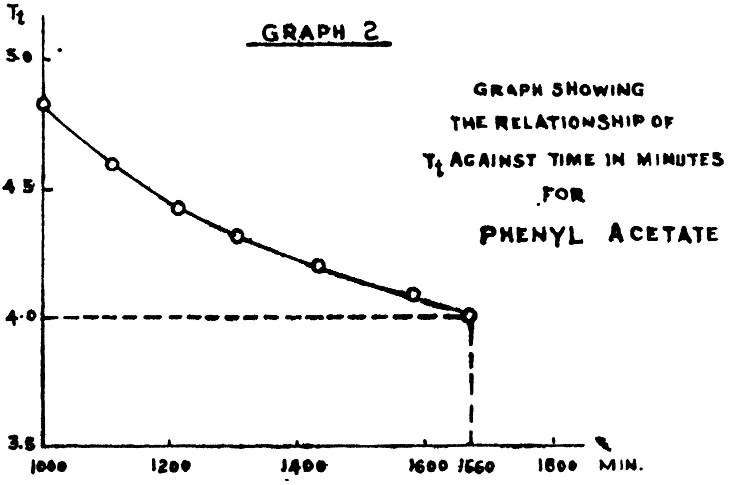
The ratio is approximately 28, which is also shown by Graphs I and II.

Graph I shows that in the case of Cyclohexyl Acetate 60 minutes are required to hydrolyse a given amount of ester. Graph II shows that in the case of Phenyl Acetate 1660 minutes are required to hydrolyse the same amount of the ester. The ratio of the two times 1660/60 is about 28. (See Graphs).

GRAPH 1



GRAPH 2



As pointed out in our previous paper (*Ibid.* 76, Nov. 1941), the ratio between the Para and Meta isomers of Methyl-Cyclohexyl and Cresyl esters is nearly 10, while of Ortho esters, it is very low. The ratio between the Cyclohexyl and Phenyl esters is nearly 28 as shown by Table II. All these show that the same ratio does not exist for all groups of saturated and their completely reduced derivatives.

In Table III are given the ratios of the esters of alcohol with homologous acids.

TABLE III

Names of Esters	Saponification Constants	Ratio
$\frac{\text{Phenyl Acetate}}{\text{Phenyl Propionate}}$	$\frac{0.000155524}{0.0000672333}$	2.313
$\frac{\text{Phenyl Propionate}}{\text{Phenyl Butyrate}}$	$\frac{0.0000672333}{0.00003256}$	2.065
$\frac{\text{Cyclohexyl Acetate}}{\text{Cyclohexyl Propionate}}$	$\frac{0.0046422}{0.00188637}$	2.46
$\frac{\text{Cyclohexyl Propionate}}{\text{Cyclohexyl Butyrate}}$	$\frac{0.00188637}{0.000884064}$	2.133

Acetates (of phenyl or cyclohexyl) are saponified about twice as fast as propionates, and propionates about twice as fast as butyrates. The ratio, however, is not the same in cresyl or methyl cyclohexyl. (*Ibid.* 76).

The ratio of Cyclohexyl Butyrate to Cyclohexyl-Iso-Butyrate is $\frac{0.000884064}{0.000215624}$, *i.e.*, 4.102. This shows that a Normal ester is saponified about four times faster than its Iso derivative. We have not been able to continue this further, but we expect that in all such cases the ratio is always nearly 4.

III—Comparison of the Saponification Constants of the Phenyl Esters of Fatty Acids with those of the corresponding Esters in which one Hydrogen Atom is replaced by a Methyl Group

The object of the present investigation is to find whether there is any relationship generally existing between the Phenyl esters of fatty acids with those of the corresponding Cresyl esters and between the Cyclohexyl esters and Methyl-Cyclohexyl esters of the same fatty acids.

Tables I and II below show the ratio of the saponification constants of the Phenyl and Cresyl and Cyclohexyl and Methyl-Cyclohexyl esters.

TABLE I

Names of Esters	Saponification Constants	Ratio
$\frac{\text{Phenyl Acetate}}{\text{Ortho-Cresyl Acetate}}$	$\frac{0.0001555}{0.0002729}$	0.5698
$\frac{\text{Phenyl Acetate}}{\text{Meta-Cresyl Acetate}}$	$\frac{0.0001555}{0.0003075}$	0.5058
$\frac{\text{Phenyl Acetate}}{\text{Para-Cresyl Acetate}}$	$\frac{0.0001555}{0.0003571}$	0.4354

TABLE I—*contd.*

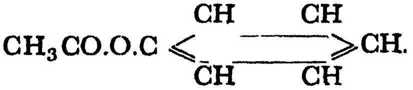
Name of Eastes	Saponification Constants	Ratio
Phenyl Propionate	0.00006723	0.5319
Ortho-Cresyl Propionate	0.0001264	
Phenyl Propionate	0.00006723	0.5892
Meta-Cresyl Propionate	0.0001141	
Phenyl Propionate	0.00006723	0.5400
Para-Cresyl Propionate	0.0001245	
Pheny Butyrate	0.00003256	0.3603
Ortho-Cresyl Butyrate	0.00009037	
Phenyl Butyrate	0.00003256	0.4777
Meta-Cresyl Butyrate	0.00006817	
Phenyl Butyrate	0.00003256	0.4203
Para-Cresyl Butyrate	0.00007737	

TABLE II

Names of Esters	Saponification Constants	Ratio
Cyclohexyl Acetate	0.004642	5.199
Ortho-Methyl Cyclohexyl Acetate	0.0008929	
Cyclohexyl Acetate	0.004642	1.467
Meta-Methyl Cyclohexyl Acetate	0.003164	
Cyclohexyl Acetate	0.004642	1.309
Para-Methyl Cyclohexyl Acetate	0.003545	
Cyclohexyl Propionate	0.001886	6.053
Ortho-Methyl Cyclohexyl Propionate	0.0003116	
Cyclohexyl Propionate	0.001886	1.669
Meta-Methyl Cyclohexyl Propionate	0.001130	
Cyclohexyl Propionate	0.001886	1.510
Para-Methyl Cyclohexyl Propionate	0.001249	
Cyclohexyl Butyrate	0.0008841	4.766
Ortho-Methyl Dyclohexyl Butyrate	0.0001855	
Cyclohexyl Butyrate	0.0008841	1.134
Para-Methyl Cyclohexyl Butyrate	0.0007797	

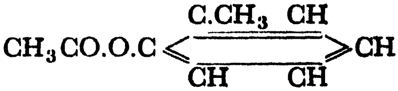
The results of the two Tables indicate that the influence on the rate of the velocity of aponification of an ester in which a methyl group has replaced a hydrogen atom in the case of Phenyl and Cyclohexyl nuclei is not the same. Thus in the following pairs of esters :—

Phenyl Acetate



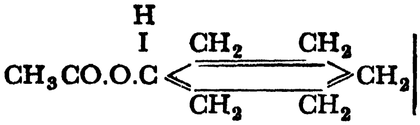
$$\mathrm{CH_3CO.O.C} < \begin{matrix} \mathrm{CH} & = & \mathrm{CH} \\ \mathrm{CH} & - & \mathrm{CH} \end{matrix} > \mathrm{CH.}$$

Ortho Cresyl Acetate



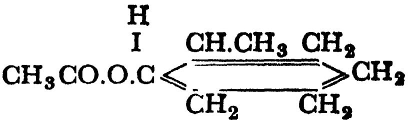
$$\mathrm{CH_3CO.O.C} < \begin{matrix} \mathrm{C.CH_3} & = & \mathrm{CH} \\ \mathrm{CH} & - & \mathrm{CH} \end{matrix} > \mathrm{CH}$$

Cyclohexyl Acetate



$$\mathrm{CH_3CO.O.}\overset{\overset{\mathrm{H}}{\mathrm{I}}}{\mathrm{C}} < \begin{matrix} \mathrm{CH_2} & - & \mathrm{CH_2} \\ \mathrm{CH_2} & - & \mathrm{CH_2} \end{matrix} > \mathrm{CH_2}$$

Ortho-Methyl Cyclohexyl Acetate



$$\mathrm{CH_3CO.O.}\overset{\overset{\mathrm{H}}{\mathrm{I}}}{\mathrm{C}} < \begin{matrix} \mathrm{CH.CH_3} & - & \mathrm{CH_2} \\ \mathrm{CH_2} & - & \mathrm{CH_2} \end{matrix} > \mathrm{CH_2}$$

it should be expected that since a Methyl group has replaced a hydrogen atom both in the Ortho-Cresyl and Ortho-Methyl Cyclohexyl Acetates in Phenyl and Cyclohexyl nuclei, the effect on the rate of saponification should be of the similar nature. As a matter of fact Ortho-Cresyl Acetate ($K=0.0002729$), Meta-Cresyl Acetate ($K=0.0003075$), and Para-Cresyl Acetate ($K=0.0003571$), are all hydrolysed more quickly than Phenyl Acetate ($K=0.0001555$), but Ortho-Methyl Cyclohexyl Acetate ($K=0.0008929$), as well as Meta and Para Methyl Cyclohexyl Acetates, are saponified much less rapidly than Cyclohexyl Acetate ($K=0.004642$). The same is the case with the esters of Propionic and Butyric acids. In other words the effects of the substitution of a Methyl group in the Phenyl nucleus is to accelerate the reaction, while in the Cyclohexyl nucleus it is to retard it. Whether this is due to the acidic nature of Cresyl nucleus as compared with the neutral behaviour of Methyl-Cyclohexyl nucleus is difficult to say in the present state of knowledge.

Tables I and II further show that there is no regular relationship with the two groups of Methyl substituted esters. The ratio of Phenyl to Cresyl esters ranges from 0.36 to 0.59, while that of Cyclohexyl and Methyl Cyclohexyl esters ranges from 1.1 to 6.

The authors take the opportunity of thanking Dr. J. V. Lakhani for valuable suggestions in the course of the above work.

CHEMICAL LABORATORY,
D. J. SIND COLLEGE, KARACHI.

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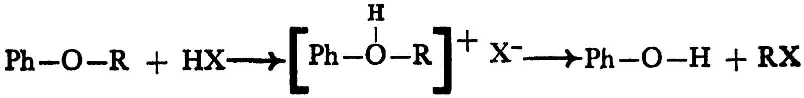
VAPOUR PRESSURES OF HALOGEN ACIDS

In Non-Polar Solvents and in Solutions of Aromatic Ethers in Non-Polar Solvents

By

S. P. WALVEKAR, N. L. PHALNIKAR AND B. V. BHIDE

THE subject of hydrolysis of ethers has been studied considerably during recent years. The mechanism of the fission of aromatic ethers with halogen acids is generally represented by the following equation :—



$$\mathrm{Ph{-}O{-}R} + \mathrm{HX} \longrightarrow \left[\mathrm{Ph{-}\overset{\overset{\displaystyle H}{|}}{O}{-}R}\right]^{+} \mathrm{X}^{-} \longrightarrow \mathrm{Ph{-}O{-}H} + \mathrm{RX}$$

where Ph=aryl radical, R=alkyl radical and X=halogen atom.

The formation of the oxonium salt —*complex*—between the ether and the halogen acid is assumed to be instantaneous and the decomposition of the complex is the rate determining factor. (*Cf.* Ghaswalla and Donnan, J. C. S., 1341, 1936 ; Bapat and Kolhatkar, J. Univ. Bom., Vol. VII, 157, 1938, etc.).

In the present work attempt was made to obtain evidence for the formation of the oxonium salt —*complex*—between halogen acids and aromatic ethers studied by Ghaswalla and Donnan (*loc. cit.*). It was thought that such complex formation could be determined quantitatively by the determination of vapour pressures of a solution of the two reactants, since one of the reactants (the halogen acid) is a gas at room temperature. The solubility of the halogen acids in benzene, carbon tetrachloride and hexane is small at room temperatures and hence the reaction between the halogen acid and the solvent must be small. These solvents were used and the vapour pressures of hydrogen chloride and hydrogen bromide were measured in the presence of different substituted anisoles.

EXPERIMENTAL

Materials :—

All the substances were either purchased from Kahlbaum or prepared in the laboratory. These were carefully purified by standard methods and used. The following table gives the physical properties of the substances. In column 2 of the table the properties given in Heilbron's Dictionary of carbon compounds are listed for comparison. The boiling points are for a pressure of 710 mm.

TABLE

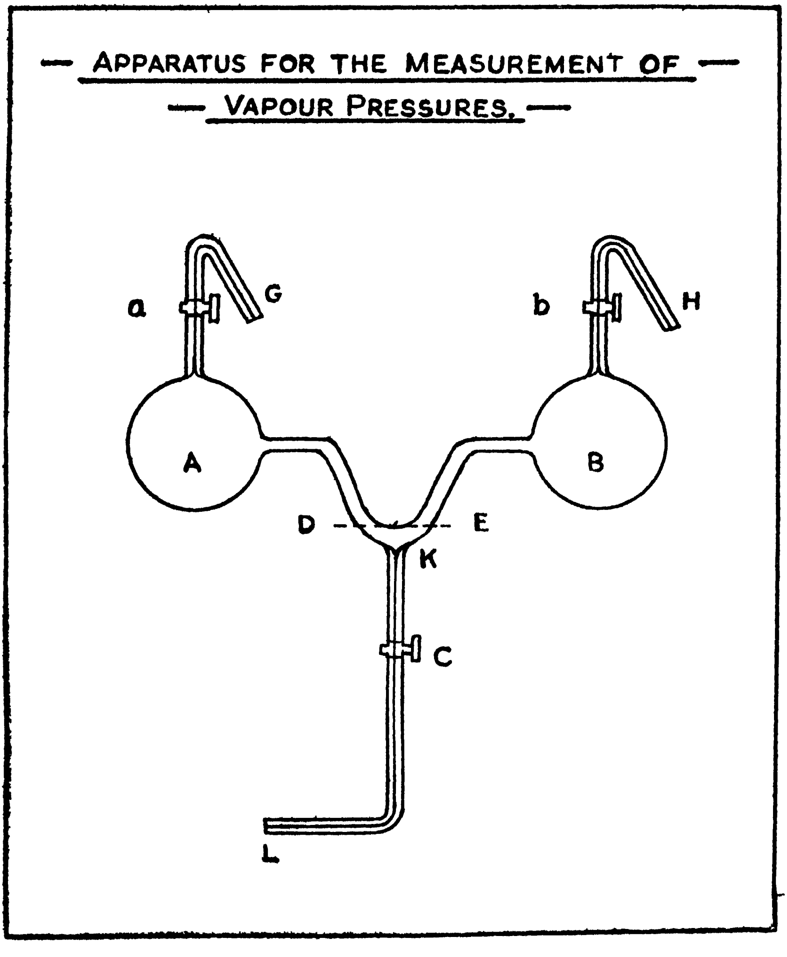
Substance	B. P. (Heilbron)	B. P. (Present Work)
Anisole	155°C	152—153°C
p-Chloro anisole	198°C	196—197°C
p-Bromo anisole	215°C	212—214°C
o-Nitro anisole	272°C	177—178°C (30 mm.)
p-Methyl anisole	175—176°C	172—173°C
Benzene	80°C	78—78.5°C
Carbon tetrachloride	76.74°C	74 5—75°C
Hexane	68.4—68.8°C	67—67.5°C

p-Nitro anisole melted at 54°C (Heilbron 54°C).

Apparatus :—

The apparatus used for the determination of vapour pressures was an improved form of the one used by Saylor (J.A.C.S. *59*, 1712, 1937). Fig. 1 gives a sketch of the apparatus.

Fig. 1



The bulbs A and B were of about 150 c.c. capacity. They were connected by the Tube D K E of about 1 cm. diameter. This was joined to a capillary stopcock at K. This stopcock was connected to a mercury reservoir at L. The bend D. K E served the purpose of separating the two bulbs A and B by raising the mercury reservoir and bringing the mercury level to D E. The volume of the bulb A, from the mark D to the stopcock 'a,' was measured by filling it with water and weighing the water.

All the measurements were carried out at 25°C in an electrically controlled airbath. As the temperature of the bath was very near the room temperature, opening the bath now and then for adjustments did not disturb the thermostatic arrangement appreciably.

The apparatus was mounted on a wooden stand and could be tilted through 90° whenever required. It could be also taken out from the stand either for shaking or for cleaning purposes. It was cleaned by chromic acid and distilled water, and was dried by a stream of dry air.

At H a bottle was connected by means of a stopper with two bent tubes, one of them was connected with a phosphorus pentoxide drying tube and the other connected to a source of the dry halogen acid. About 25 c.c. of the solvent was introduced into the bottle and the halogen acid passed in till the required concentration was reached.

As soon as the solution was ready the capillary tube was filled with mercury up to K by raising the reservoir. Stopcock C was then closed, 'a' was opened and a slight suction was applied at G through a calcium chloride tube. The stopcock was opened and the solution was allowed to enter the bulb B. 'b' was closed and the liquid transferred from B to A and back several times. It was thus possible to get the equilibrium between vapour and solution quickly. O'Brien, Kenny and Zuercher (J.A.C.S. *61*, 2504, 1939) who used Saylor's apparatus, state that the equilibrium was obtained in 24 hours. In our apparatus this time is reduced to less than 20 minutes. Preliminary experiments showed that the ethers were not decomposed during this period. After thorough shaking, the liquid was divided between the bulbs A and B and allowed to stand in the thermostat. After 10 minutes the apparatus was tilted through 90° so as to transfer all the solution from A to B. It was allowed to rest in this position for some time so as to allow the solution to drain into B completely. The apparatus was then brought back to its original position, the stopcock C opened and the mercury gradually raised till it came to the level D E. Then stopcock 'a' was opened, the end G dipping into a beaker containing water, the vapour in A was gradually displaced up to 'a' by the mercury into the water. The halogen acid thus absorbed in water was titrated by standard alkali. The solution in B was likewise transferred to another weighed bottle containing water. The bottle was weighed and the acid estimated by standard alkali. All the concentrations are expressed as mols. of halogen acid per 1000 gms. of solvent.

The apparatus is not capable of giving results of high accuracy. However it was found that the results were reproducible to within 1 to 2%.

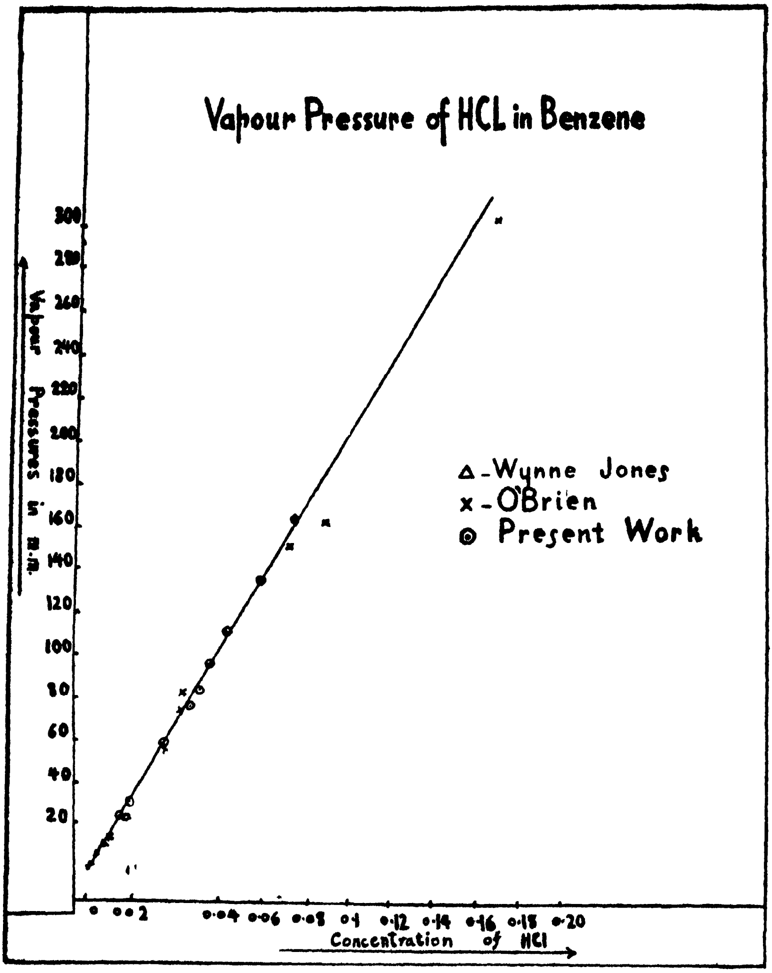
RESULTS AND DISCUSSION

The following table gives the vapour pressures of hydrogen chloride in benzene. All vapour pressures (p) are given in mm. of mercury and concentration (c) in gram mols. per 1000 gms. of solvent.

TABLE

c	0.01830	0.02273	0.03931	0.05043	0.6052
p	29.5	34.8	61.8	78.5	97.5
c	0.06754	0.08283	0.09768		
p	111.4	134.2	161.5		

Fig. 2



These values are plotted in Fig. 2 together with the values of Wynne-Jones (J. C. S. 1064, 1930) and O'Brien *et al.* (J. A. C. S. *61*, 2504, 1939). It will be seen that there is good agreement between the values of these authors and our values.

Vapour pressures of hydrogen chloride in benzene in the presence of anisole, p-Methoxy anisole and p-Nitro anisole were determined. The results are given below.

0.1 mol. anisole per 1000 gms. of benzene

c	.03755	0.04726	0.06716	0.08112	0.9707
p	53.7	61.4	91.4	113.2	143.4
c	0.1521				
p	225.3				

0.1 mol. of p-methoxy anisole per gms. of benzene

c	0.05446	0.05718	0.08588	0.1163	0.1214
p	86.4	87.4	131.2	187.7	197.1

0.1 mol. of p-nitro anisole per 1000 gms. of benzene

c	0.06125	0.09215	0.1035	0.1307
p	95.3	148.9	174.4	215.9

A lowering of vapour pressure was observed only in the presence of anisole while in the case of the other two ethers the vapour pressure was the same as in the pure solvent. No indication was thus obtained of a complex formation between ethers and hydrogen chloride. It was thought that this negative result was due to the interaction of solvent and the halogen acid (*vide* O'Brien *et al., loc. cit.*). Further experiments were tried in solutions of carbon tetrachloride and hexane in the presence of ethers and hydrogen chloride or hydrogen bromide.

The results are summarised below :—

v. p. of HCl in carbon tetrachloride

c	0.00828	0.01084	0.01353	0.01894
p	59.5	69.9	98.56	133.20
c	0.02278	0.02460	0.02859	
p	154.2	167.9	188.2	

v. p. of HBr in carbon tetrachloride

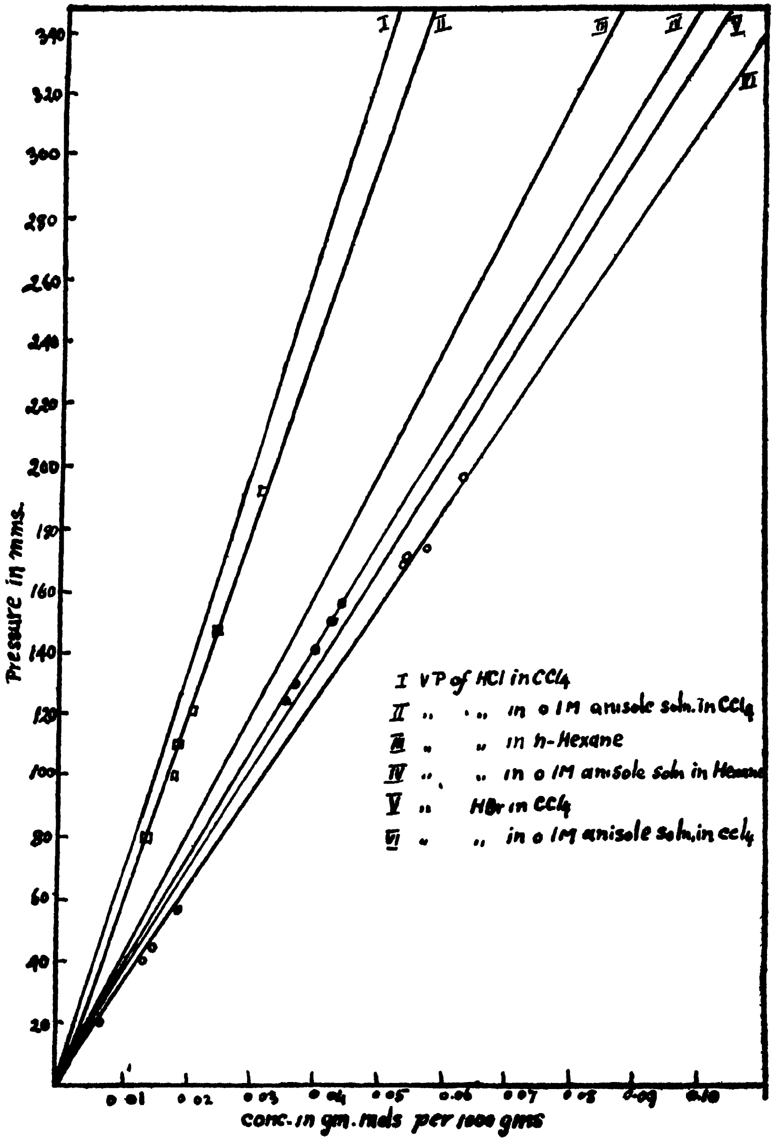
c	0.01671	0.0194	0.02944	0.03654	0.04750
p	57.0	64.2	96.25	121.8	153.2
c	0.05206	0.0622			
p	172.2	210.9			

v. p. HCl in n-hexane

c	0 01844	0.02424	0.03610	0.03984	0.04306
p	68.3	98.2	143.6	153.9	172.2

On plotting these results it was found that Henry's Law was obeyed and there was a positive deviation from Rault's Law.

Fig. 3



The following table gives the vapour pressures of hydrogen chloride in carbon tetrachloride with varying concentration of anisole.

0.1 mol. anisole/1000 gms. of solvent

c	0.01341	0.01763	0.01968	0.02463	0.03133
p	80.4	110.1	119.5	145.9	192.7

0.18 mol. anisole/1000 gms. of solvent

c	0.01788	0.01891	0.02156	0.02552	0.02721
p	97.3	108.5	116.40	139.4	156.30

0.3 mol. anisole/1000 gms. of solvent

c	0.01693	0.02208	0.02381	0.02789	0.02977
p	90.4	115.7	125.6	144.7	149.4

0.5 mol. anisole/1000 gms. of solvent

c	0.02595	0.02913	0.03031	0.03174	0.03810
p	117.1	140.2	145.5	152.6	176.2

The results show (Fig. 3) that there is a lowering of vapour pressure due to the presence of anisole in each case. The lowering may be due to complex formation between anisole and hydrogen chloride. Attempt was made to calculate the equilibrium constant (K) of such a complex.

$$K = \frac{C_{\text{complex}}}{C_{\text{free HCl}} \times C_{\text{free anisole}}}$$

Similar experiments were carried out with other ethers. The results are summarised in the following table.

Solvent :—Carbon tetrachloride.

TABLE

Ether	K for 0.1 mol. ether	K for 0.18 mol. ether	K for 0.3 mol. ether	K for 0.5 mol. ether
Anisole	1.51	1.33	1.10	0.93
p-Chloro anisole	0.58	....	0.55	0.57
p-Nitro ,, ...	1.51	....	1.38	1.22
p-Methoxy ,, ...	2.65	....	2.08	....
p-Methyl ,, ...	2.44	....	1.24	1.62
o-Nitro ,, ...	0.429	....	....	0.973
m-Methoxy ,, ...	1.133	....	....	0.88

It will be observed that the values of K vary for different concentrations of the ether. The values of 1/K vary rectilinearly with the concentration and the variation is too large to be due to experimental errors. To get comparable values of K, values of 1/K were extrapolated to zero concentration of the ethers. These are given in the following table along with the velocity coefficients of hydrolysis of ethers obtained by Ghaswalla and Donnan (*loc. cit.*).

TABLE

Ether	K	Velocity Coefficient 10^4
p-Methoxy anisole	3.12	339
p-Methyl „	2.86	102
Anisole	1.72	71.4
p-Nitro anisole	1.56	6.89
m-Methoxy „	1.22	187.0
o-Nitro „	0.379	7.28

It will be seen that there is no connection whatsoever between the equilibrium constants and velocity constants. If the equilibrium constant is proportional to the concentration of the oxonium salt such a relationship should have been observed.

Similar experiments were carried out with Hydrogen bromide in hexane and carbon tetrachloride solutions. The results were quite analogous.

These experiments do not give any quantitative idea of the extent of complex formation. Probably complex formation is masked by other factors such as solvent effects, etc.

MAHARAJA PRATAPSINH
CHEMICAL LABORATORY,
SIR PARASHURAMBHAU COLLEGE,
POONA

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HEAT POLYMERISATION OF TRIGLYCERIDES

Part I—Tristearin and Triolein

By

N. L. Phalnikar and B. V. Bhide

IT is a well-known fact that oils on heating give polymerised products particularly when linolic and linolenic acids form part of the constituent acids. The products of such polymerisation are boiled oils and stand oils which are of great commercial importance.

During recent years attempts have been made to study the nature of these products by chemical analysis. The work of Kino. K., [Sci. Papers, Inst. Phys. Chem. Research (Tokyo), *26*, 91, (1935); *ibid.*, *30*, 244, (1936)], Steger, A., and Loon, J. van, [Rec. trav. chim., *54*, 756, (1935); *54*, 428, (1935)] and Bradley and co-workers [Ind. Eng. Chem., *32*, 802, (1940)] appears to be of great importance. They have studied the effect of heat on several methyl esters of unsaturated acids and have studied the nature of the resulting polymerised products.

We have studied the thermal polymerisation of a number of vegetable oils such as niger seed oil, safflower oil, olive oil, etc., and have analysed completely the polymerised products as well as the distillate (unpublished work). The products obtained, however, were of such a great complexity that it was difficult to give a rational interpretation of the mechanism of the process. It appeared to us, therefore, that the interpretation of the results would be much simplified if pure synthetic glycerides were heated to suitable temperatures and the products chemically identified.

Previous workers have carried out the thermal polymerisation in the presence of inert gases to avoid oxidation. In our experiments the heat treatment of the glycerides was carried out in vacuum and the residue as well as the distillate have been subjected to a thorough chemical analysis. The only work which has been done on similar lines is the work of Simons (J.A.C.S., *48*, 1991, 1926). This author has examined the products of decomposition at atmospheric pressure of triacetin and tripropionin in the presence of thorium oxide.

In this communication we have described the thermal decomposition of tristearin and triolein. The mechanism of decomposition will be described in a later communication.

EXPERIMENTAL

Tristearin was prepared by the method recommended by Clarkson and Malkin. (J.C.S 1934, 666).

Triolein was prepared by heating U.S.P. oleic acid having the theoretical iodine value with glycerine at 125°C in the presence of *p*—toluene sulphonic acid as a catalyst. The oleic acid was guaranteed free from linolic acid. The triolein gave the correct iodine value and saponification value and had negligible acid value (1).

The glycerides were heated in an ordinary flask with three bulbs and the distillate and the residue were analysed by the usual methods. During heating a considerable amount of acrolein with small quantities of carbon dioxide was obtained.

TRISTEARIN

(With Mr. Y. V. Duvedi)

Distillation of tristearin :—

Tristearin (m.p. 70—71°C) (100 gms.) was distilled under reduced pressure (30 mm.). The temperature of the liquid never exceeded 410°C. Almost all the tristearin distilled over leaving very little residue (3 gms.). During distillation a large amount of acrolein and a small quantity of carbon dioxide were given out. The distillate (87 gms.) was a solid and had the following constants :—

Acid value	=103.1
Saponification value	=218.0
Iodine value	= 4.0

Analysis of the distillate :—

The distillate was taken up in a large volume of ether and the acid was separated by treatment of the ethereal extract with sodium carbonate and was identified as stearic acid by its m.p. 69—70°C, equi. wt. 284.6 and mixed m.p.

The ether extract on removal of the acid, gave on evaporating ether, a neutral product, which had no iodine value and had a saponification value 90 and a mean mol. wt. 677. The acid obtained from the neutral product by saponification was identified as stearic acid. Portion of the neutral product easily soluble in alcohol was identified by its melting point 71—72, saponification value 194 and mean mol. wt. 850 as tristearin. The portion sparingly soluble in alcohol had mol. wt. 480 and was identified as stearone by mixed m.p. 89 (a pure specimen of stearone was prepared for this purpose according to the method of Easterfield and Taylor (J.C.S., *99*, 2800, 1911).

The distillate, therefore, contains 52% stearic acid, 22% tristearin and 26% stearone.

TRIOLEIN

(With Mr. R. C. Shah)

Distillation of triolein :—

Triolein was distilled under reduced pressure (30 mm.) in the same way as in the case of tristearin. A thermometer, kept in the liquid, showed that the temperature was between 350—360° during the process. If the temperature is allowed to rise above 360° carbonisation takes place. The heating was discontinued as soon as there was a sign of increase of temperature above 360° when volatile material stopped coming over. From 87 gms. of triolein 40 gms. of the distillate and 40 gms. of the residue were obtained. These were analysed separately.

Analysis of the distillate :—

The distillate had the following constants :—

Acid value	=147.5
Iodine value	= 78.5
Saponification value	= 23.0

It was separated into the free acid and the neutral portion by treatment with sodium carbonate.

The acid portion on subjecting to steam distillation gave a steam volatile acid which had equi. wt. 155, and had no iodine value and hence it was identified as pelargonic acid $C_9 H_{18} O_2$ ($C_9 H_{18} O_2$ requires equiv. wt. 158).

The steam nonvolatile acid had equiv. wt. 287 and Iodine value 88 and was therefore identified as oleic acid which was further confirmed by its oxidation to dihydroxy stearic acid (m.p. 131°C).

The neutral portion from the distillate :—

This had iodine value 87 and saponification value 140.5. The neutral portion on saponification gave an acid which was identified as oleic acid by its equiv. wt. 277, iodine value 90 and oxidation to dihydroxy stearic acid (m.p. 131°C). The unsaponificable neutral portion contained mostly hydrocarbons and traces of ketones as it gave a small quantity of a semicarbazone without a definite melting point. This portion absorbed bromine readily and therefore unsaturated hydrocarbons must be present.

The distillate, therefore, consists of pelargonic acid, oleic acid, unchanged triolein, hydrocarbons and traces of ketones.

Analysis of the residue :—

The residue (40 gms.) had the following constants :—

Saponification value	=173.0
Iodine value	= 80.5

This was refluxed with 300 c.c. of acetone in three 100 c.c. lots and separated into the acetone soluble portion (A) and acetone insoluble portion (B).

Analysis of the acetone soluble portion (A) :—

The constants of this fraction are as follows :—

Acid value = 23.5
Saponification value =207.5
Iodine value = 68.0

The whole lot was saponified and the liberated acids, which were semi solid, were again separated into solid and liquid acids by the lead salt alcohol method. The first fraction of the lead salt was a semi solid. This was again subjected to the same process but it could not be obtained in a crystalline form. The acids from this fraction gave the following constants :—

Equi. wt. = 297.
Mol. wt. = 553.
Iodine value = 68.

The acid is evidently polymerised oleic acid.

After the separation of these lead salts a fraction of crystalline lead salt was obtained on cooling to 10°C. These solid acids still showed some iodine value and therefore were again separated by the same method. The liquid acids combined together gave an equi. wt. 280 and iodine value 83. This was identified as oleic acid by oxidation to dihydroxy stearic acid (m.p. 131°C). The solid acid from the crystalline lead salts on recrystallisation from benzene was found to be sebacic acid (m.p. 133°C). (Mixed m.p. with an authentic specimen showed no depression. Equi. wt. 102. $C_{10} H_{18} O_4$ requires 101).

Analysis of the acetone insoluble portion (B) :—

The acetone insoluble part (B) had iodine value 85.6, saponification value 175.6 and acid value 1.3. This was saponified by alcoholic potash. The soap was extracted with ether. The extract gave a trace of a liquid but the quantity being very little it could not be further analysed. The soap was dissolved in water and acidified and the acids were removed by ether. The aqueous layer was concentrated on the water bath and treated with anhydrous sodium sulphate and was extracted with acetone. On removal of acetone a viscous liquid was obtained which gave acrolein on heating with potassium hydrogen sulphate and the colour reaction with phenol and conc. sulphuric acid for glycerine. (*Cf.* Allen's Commercial Organic Analysis, 5th edition, Vol. II, p. 654). This viscous liquid was, therefore, glycerine.

20 gms. of the above acids were converted into the methyl esters. These were fractionally distilled at 25 mm. and they had the following constants :—

Fraction	B.P.	Wt.	Equi. wt. of the corresponding acid	I.V.	Refractive Index
1	up to 220	3.5	....	nil	1.4400
2	220—240	3.5	259.5	65.8	1.4492
3	240—275	3.5	282.0	71.9	1.4597
Residue		9.5	....	....	....

1st Fraction :—

This was hydrolysed and the acids liberated. The product was a solid at room temperature but contained a small quantity of a liquid as an impurity. It was, therefore, washed with a small quantity of petrol. A white solid acid was obtained having an equi. wt. 110 and m.p. 124—127°C. It was then crystallised from alcohol when it melted at 133—134°C and had equi. wt. 103 and mol. wt. (Rast's method) 201. Mixed melting point with an authentic specimen of sebacic acid showed no depression. (Sebacic acid requires equi. wt. 101 and mol. wt. 202 and m.p. 133—134°C). The petrol washings on evaporation left a small quantity of a liquid which was not investigated.

2nd Fraction :—

The liberated acid from this fraction was a semi-solid and had equi. wt. 259.5 and I. V. 65.8. Attempts to separate these by fractional crystallisation were unsuccessful. The acids were, therefore, separated into liquid and solid acids by lead salt alcohol method.

The liquid acid had equi. wt. 280 and I. V. 80. This must be, therefore, largely oleic acid which was further confirmed by its oxidation to dihydroxy stearic acid (m.p. 131°C). The solid acids obtained from the above separation had equi. wt. 231.3 and mol. wt. 443, I. V. 61. It could not be obtained in a crystalline form and was gummy.

3rd Fraction :—

The acids isolated from this fraction were viscous and brown in colour. These were separated by the lead salt alcohol method. The first crop of the lead salt was a viscous semi-solid mass. This was separated and was found to have equi. wt. 298.4, mol. wt. 539.0 and I. V. 73.

The mol. wt. is not a simple multiple of the equi. wt. and therefore this must be a mixture. The quantity was too small for further separation. The liquid acids gave an equi. wt. 282 and I. V. 86.5. This must be, therefore, oleic acid.

The Residue :—

The acids (6 gms.) were liberated and freed fromn eutral portion. It was a dark viscous mass and had equi. wt. 358, mol. wt. 634 and I. V. 76.8.

SUMMARY

Synthetic tristearin and triolein have been heated in vacuum and the residue and the distillate analysed. In each case a large amount of acrolein with a small quantity of carbon dioxide was given out.

Tristearin on distillation gave a negligible residue and a distillate which was found to contain stearic acid (58%), unchanged tristearin (22%) and stearone with traces of hydrocarbons (26%).

The distillate from the heat treatment of triolein was found to contain pelargonic acid, oleic acid, unchanged triolein and hydrocarbons with traces of ketones.

The residue obtained from the heat treatment of triolein was separated into two fractions : (1) Acetone soluble part, (2) acetone insoluble part.

(1) The acetone soluble part on saponification was found to contain sebacic acid, oleic and polymerised acids (mol. wt. 553).

(2) The acetone insoluble portion on saponification gave glycerine sebacic acid, oleic and polymerised acids (probably mixtures). Mol. wts., 443, 539, and 634.

Acids of high mol. wt. and also of low mol. wt. have been obtained from triolein. Tristearin, however, gave only stearic acid.

A mechanism of the decomposition will be described in a later communication when the results of heat treatment of triglycerides of diethenoid acids like linolic acids will be ready. Work on these lines is in progress.

MAHARAJA PRATAPSINHA
CHEMICAL LABORATORY,
SIR PARASHURAMBHAU COLLEGE,
POONA

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ACTION OF SULPHURYL CHLORIDE AND DIAZOBENZENE CHLORIDE ON SOME AROMATIC THIOETHERS

By

A. V. Rege, J. W. Airan, and S. V. Shah

RECENTLY thioethers of the general formula R-S-R (where R represents $\overset{[3]}{COCH_3}.\overset{[4]}{OH}.\ C_{10}H_6-$; $\overset{[2]}{OH}.\ C_{10}H_7-$; $\overset{[4]}{OH}.\ \overset{[3]}{COOH}.\ C_{10}H_6-$; and $\overset{[2]}{OH}.\ \overset{[3]}{COOH}.\ C_{10}H_6-$) have been prepared by Airan and Shah (J. Univ. Bom., 1940, *9*, *iii*, 115). In these thioethers the sulphur linkage is stable towards cold alkali, dilute hydrochloric acid, and boiling acetic anhydride. To determine the position of sulphur atom in the thioethers, the compounds were broken up by treatment with nitric acid or bromine (*Ibid*, p. 117) and from the position of the nitrogroup or bromine atom, the position of the sulphur atom was settled.

In the light of these results, it was found interesting to investigate how sulphuryl chloride and diazobenzene chloride would react with these thioethers. It is already known that sulphuryl chloride acts as a chlorinating agent when allowed to react with 2–acetyl- α -naphthol ; 1:2-oxynaphthoic acid ; 2:3–oxynaphthoic acid (Airan and Shah : J. Univ. Bom., 1942, *10*,*v*, 133) and with β–naphthol (Armstrong and Rossiter : Chem. News, *59*,225). [By the way, the ease with which chlorination is brought about with sulphuryl chloride, is indicated by the formation of α -chloronaphthalene and 1 : 4–dichloronaphthalene (see experimental part of this communication) from naphthalene and sulphuryl chloride under the normal conditions available in the laboratory].

In the case of diazobenzene chloride, it is well known that it couples well with naphthols and their derivatives.

The compounds included in this investigation are :—

3,3′–diacetyl–4,4′–diphydroxy-dinaphthyl sulphide,
2,2′–dihydroxy-dinaphthyl sulphide,
3,3′–dicarboxy–4,4′–dihydroxy–dinaphthyl sulphide,
and 2,2′–dihydroxy–3,3′–dicarboxy–dinaphthyl sulphide.

With sulphuryl chloride, it was found that, except in the case of the thioether of 2 : 3-oxynaphthoic acid, the sulphur linkage was broken. The thioethers of 2-acetyl-α-naphthol and 1 : 2-oxynaphthoic acid gave corresponding chloro-derivatives, whereas the thioether of β-naphthol gave a plastic mass from which neither the original thioether nor any crystalline solid could be isolated.

Also, as a result of the interaction between the thioethers and diazobenzene chloride, the sulphur linkage was broken in all the cases, the resulting compounds, except that from the thioether of 2-acetyl-α-naphthol, being the already known usual azo dyes. The dye obtained as a result of the breaking down of the thioether of 2-acetyl-α-naphthol is identical with the dye obtained directly from 2-acetyl-α-naphthol by similar treatment. This was proved by nitrogen estimation and mixed melting point. Evidently, the azo group is in 4-position, which was occupied by the sulphur atom in the thioether. (Airan and Shah: J. Univ. Bom., 1940, *9*, *iii*, 117).

The position which the chlorine atom in the chloro-compound of 2-acetyl-α-naphthol was assigned, was by analogy with Hantzsch's 4-bromo-2-acetyl-α-naphthol. (Airan and Shah: J. Univ. Bom., 1942, *10*, *v*, *132*). But it is now confirmed, since, evidently, when sulphuryl chloride broke down the thioether of 2-acetyl-α-naphthol, the chlorine atom took the place of the sulphur atom, namely the 4-position.

The results are very interesting in view of the fact that though the coupling reaction takes place in all the cases at low temperature, breaking down the sulphur linkage, the thioether of 2 : 3-oxynaphthoic acid remains unaffected even on being refluxed with sulphuryl chloride for three hours. On the whole these reactions have afforded additional proof regarding the position of the sulphur atom in the thioethers.

EXPERIMENTAL

(The experimental part of this work was carried out by Mr. Rege.
—S.V.S.)

1. *Reaction with diazobenzene chloride.*

50 per cent. HCl (40 cc) was added to about 10 cc of freshly distilled aniline, and kept in ice. Then a 50 per cent. aqueous solution of sodium nitrite was run into it till a drop of the reaction mixture gave an immediate coloration with starch-iodide paper. This diazo mixture was then gradually added with constant stirring, to a solution of the thioether in sodium hydroxide, also kept in ice. By way of precaution, a bit of urea was added. The dyes isolated were purified by crystallization from acetic acid.

Thioether	Dye obtained and Melting Point	Mixed Melting Point with the dye obtained for comparison
3, 3'-diacetyl-4, 4'-dihydroxy-dinaphthyl sulphide	4-benzeneazo-2-acetyl-α-naphthol 136°C	136°C Prepared for the first time. Found · N, 9.34, $C_{18}H_{14}O_2N_2$ requires 9.59 per cent.

Thioether	Dye obtained and Melting Point	Mixed Melting Point with the dye obtained for comparison
2, 2′-dihydroxy-dinaphthyl sulphide	1-benzeneazo-β-naphthol 134°C	134°C (Ber., *16*, 2858)
3, 3′-dicarboxy-4-, 4′-dihydroxy-dinaphthyl sulphide	4-benzeneazo-1-oxy-2-naphthoic acid 192°C	192·194°C (Ber., *20*, 1275)
2, 2′-dihydroxy-3, 3′-dicarboxy-dinaphthyl sulphide	1-benzeneazo-2-hydroxy-3-naphthoic acid 230°C	230·232°C (Ber., *26*, 289)

2. *Reaction with sulphuryl chloride.*

The thioether (2g.) was taken in 25 cc dry benzene in a round bottom flask, and sulphuryl chloride was added gradually (10 cc) with constant shaking, and then the reaction mixture was refluxed on a water bath for an hour. The solvent was distilled off and the residue crystallized from alcohol.

Thioether	Chloro derivative	Mixed Melting Point with the chloro-compound prepared for comparison
3, 3′-diacetyl-4, 4′-dihydroxy dinaphthyl sulphide	4-chloro-2-acetyl-α-naphthol 116°C	116°C (J. Univ. Bom., 1942, *10*, *v*, 132)
2, 2′-dihydroxy-dinaphthyl sulphide	Plastic mass from which no crystalline product could be obtained	
3, 3′-dicarboxy-4, 4′ dihydroxy-dinaphthyl sulphide	4-chloro-1-hydroxy-2-naphthoic acid 229°C	229°C (Ber., *44*, 3061)
2, 2′-dihydroxy-3, 3′-dicarboxy-dinaphthyl sulphide	No reaction even after refluxing for three hours	

3. *α-chloronaphthalene.*

Naphthalene (5 g.) was dissolved in ether and after adding 2 cc sulphuryl chloride, the reaction mixture was kept aside overnight. Next day, finding that no solid had fallen out, the mixture was poured in cold water and again left overnight. Next day a viscous mass was formed at the bottom. This was taken up with ether and left overnight, when a white crystalline solid appeared along with a liquid product. The solid and the liquid products, separated after rapid and repeated treatment with ether, were found to be in the proportion of 1 to 5 respectively.

The liquid product contained chlorine and no sulphur. Its boiling point was 257 °C, 259 °C being the boiling point of the only mono-chloro derivative of naphthalene, which is ∝-chloronaphthalene, and which was obtained by Tohl and Eberhard (Ber., 1893, *26*, 2945) by treating naphthalene with sulphuryl chloride in the presence of aluminium chloride.

Found : Cl, 21.81 ; $C_{10}H_7Cl$ requires 21.85 per cent.

4. *1:4-dichloro-naphthalene.*

The solid product mentioned above was crystallized from ether. It contained chlorine and no sulphur. It melted at 67–68 °C. There is no other dichloro-derivative of naphthalene recorded in literature, melting at 67-68 °C, except 1:4-dichloro-naphthalene which was prepared by Armstrong (Chem. News, *66*, 189) by treating ∝-chloronaphthalene with sulphuryl chloride at 100—180 °C. (Found: Cl, 35.97 ; $C_{10}H_6Cl_2$ requires 36.04 per cent).

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RAJARAM COLLEGE,
KOLHAPUR

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ORTHO-CRESYL BUTYRATE AND META-CRESYL BUTYRATE

Their Preparation and Properties

By

B. E. MIRZA AND G. D. ADVANI

PREPARATION

ORTHO-CRESYL Butyrate and Meta-Cresyl Butyrate were prepared by the action of the respective Cresols on Butyryl Chloride, which was prepared as follows :—

Pure Butyric acid (66 gms) (boiling between 160°—161° C) was placed in a 500 c.c. distilling flask, the side tube of which was connected to a water condenser. The receiving flask was also a distilling flask, the side tube of which was connected to a water trough in order that the fumes of HCl and PCl_3 may be absorbed by water. PCl_3 (34.4g) was added to the acid drop by drop and the mixture was allowed to stand for about 4 hours, after which it was distilled, and the Butyryl Chloride boiling between 101°—102°C was collected.

(1) PREPARATION OF ORTHO-CRESYL BUTYRATE

Ortho-Cresol (70 g) was added drop by drop from a dropping funnel to Butyryl Chloride (70 g). The bottle was shaken vigorously and kept aside for twenty-four hours for the reaction to proceed. It was then fractionally distilled under reduced pressure.

Ortho-Cresyl Butyrate distilled between 127°—128° C at 5 mm. pressure, and weighed 67.8 gms, the yield being 58.04 per cent.

(2) PREPARATION OF META-CRESYL BUTYRATE

Meta-Cresol (Poulène Frères) (70 g) was added drop by drop to Butyryl Chloride (70 g) and the process was repeated as in the last case.

Meta-Cresyl Butyrate distilled between 132°—133°C at 5 mm. pressure and weighed 84.5 gms, the yield being 72.61 per cent.

Properties

PARACHOR

In this investigation the Surface Tension has been measured by the double capillary rise method by Sugden. (Jour. Chem. Soc. 1921), 119, 1483). A set of two Capillaries of radii 0.1348 and 0.05164 Cms. formed the combination of working. The Capillaries were tested for circularity of cross-section and uniformity of bore in the manner described by Harkins. (Jour. Am. Chem. Soc. 1919, *41*, 499).

The difference in level of the rise of solution in the two Capillaries of different radii was measured by a travelling microscope fitted with a silver vernier scale reading directly up to 0.01 m.m. (Supplied by F.E. Becker & Co., Hatton Wall, London; No. 1641).

The Surface Tension was calculated by the equation

$$r = \frac{a^2gd}{2}$$

where r is the Surface Tension, a^2 the Capillary Constant, g the acceleration due to gravity and d the density. The Capillary Constant was found from the formula

$$a^2 = \frac{H}{\frac{1}{r_1} - \frac{1}{r_2}}$$

where r_1 and r_2 are the radii of the Capillaries and H the difference in height. (Sugden, *loc. cit.*). The determinations were made at different temperatures as shown in Table I, to see the correctness of the results.

The following constants were used in the calculation of the Parachors:–

$C = 4.8$, $H = 17.1$, $O = 20.0$,
Carboxyl $O_2 = 60.0$ (O_2 in esters).
Double bond = 23.2.

Six membered ring=6.1 (*Cf.* "Parachor and Velency," 1930, George Routledge & Sons, pages 38, 131, 181).

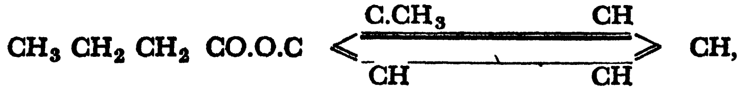
The results are given in Table I.

TABLE I

Parachor of the Two Esters

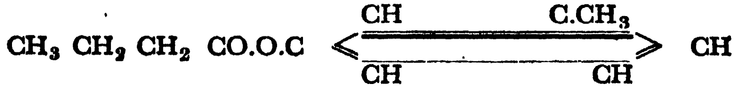
Temp.	Names of Esters	d	r	P (Obs.)	P (Cal.)
35°C.	Ortho-Cresyl Butyrate ..	1.001	32.7	425.2	427.9
26.8°C.	„ „ „ ..	1.005	33.33	425.6	427.9
35°C.	Meta-Cresyl Butyrate ..	0.9982	32.27	425.0	427.9
23°C.	„ „ „ .	1.003	33.16	425.6	427.9

The results of the Parachor in Table I prove that the Constitution of Ortho-Cresyl Butyrate is



$$CH_3\;CH_2\;CH_2\;CO.O.C < \begin{array}{cc} C.CH_3 & CH \\ \hline\hline CH & CH \end{array} > CH,$$

and the Constitution of Meta-Cresyl Butyrate is



$$CH_3\;CH_2\;CH_2\;CO.O.C < \begin{array}{cc} CH & C.CH_3 \\ \hline\hline CH & CH \end{array} > CH$$

MOLECULAR WEIGHT

In this investigation the Surface Tension was measured by the Double Capillary Rise method as in the previous case.

The Densities of solutions were measured by using a Specific Gravity bottle of 10 c.c. capacity.

The Molecular weight was calculated by using the following formula:–

$$M=\left(\frac{C(t_1-t_2)}{\dfrac{r_1}{(d_1)^{\times 2/3}}-\dfrac{r_2}{(d_2)^{2/3}}}\right)^{3/2}$$

where M is the Molecular weight, r_1 and r_2 the Surface Tensions and d_1 and d_2 the Densities at two different temperatures, t_1 and t_2 respectively, and C is a constant.

The constant C is taken as —2 . 12, as has been found in many cases.

The results are given in Table II.

TABLE II

Molecular Weight of the Two Esters

Names of Esters	Temp.	r	d	M
Ortho-Cresyl Butyrate	35°C.	32.70	1.001	187.7
„ „ „	26.8°C	33.33	1.005	
Meta-Cresyl Butyrate	35°C	32.27	0.9982	188.5
„ „ „	23°C	33.16	1.003	

So the Molecular weight of Ortho-Cresyl Butyrate is 187.7 and Meta-Cresyl Butyrate is 188.5 as compared with the value 178 calculated from the formula.

REFRACTIVE INDEX

The Refractive Index was found by the self-reading Abbe Refractometer, with water-jacketed prisms. The range of the index of refraction measurable by this instrument is from 1.3000 to 1.7000 and the accuracy of the reading was 0.0001.

It was necessary to standardise the refractometer before use. For this purpose, a standard glass test-piece is provided, the index of refraction of which is marked on it (1.5163).

All the measurements were made with artificial electric light taking only one or two drops of the liquids for each determination. The refractive index was read directly on the scale. The temperature was always maintained at 29°C.

The results are given in Table III.

TABLE III

Refractive Index of the Two Esters

Names of Esters	Index of Refraction
Ortho-Cresyl Butyrate	1.4900
Meta-Cresyl Butyrate	1.4922

VISCOSITY

The determination of the Viscosity was carried out by the Comparative Method. The apparatus employed for the determination was the Ostwald Modification of Poisouilles apparatus. The tube containing the ester was kept in the self-regulated thermostat, which was maintained at 35.0°C. It was so immersed in the thermostat as to have the upper mark well beneath the surface of the water. For determining the time of outflow, a stop-watch reading directly to 0.20 of a second was used.

The formula used to determine the Viscosity was as under :—

$$\frac{n_2}{n_1} = \frac{S_2 \ T_2}{S_1 \ T_1}$$

where n_2 is the viscosity of the liquid ; n_1 the viscosity of water (0.00724 at 35 °C: *Vide* Landolt=Borustein, Physikalisch=Chemische Tabellen, page 136, Vol. I, part 1); S_2 the density of the liquid; S_1 the density of water (0.99406 at 35 °C: *Vide* Ibid., page 73, Vol. I, part 1); T_2 the time taken by the liquid to flow from the upper mark to the next; and T_1 the time taken by water to flow between the same two marks.

The results are given in Table IV.

TABLE IV

Viscosity of the Two Esters

Names of Esters	Density	Time of Flow	Viscosity
Ortho-Cresyl Butyrate	1.001	95.4 secs.	0.02457
Meta-Cresyl Butyrate	0.9982	97.3 „	0.02500

The authors take the opportunity of thanking Dr. J. V. Lakhani for valuable suggestions in the course of the above work.

CHEMICAL LABORATORY,
D. J. SIND COLLEGE, KARACHI.

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ADDITION OF PHENOL ETHERS TO SUBSTITUTED CINNAMIC ACIDS

By

B. D. PATEL AND K. V. BOKIL

INTRODUCTION

IN an attempt at the direct synthesis of substituted cinnamic acids by the action of acetoacetic ester on phenol ethers in the presence of 80% sulphuric acid, β-β-disubstituted butyric acids were obtained instead of the expected substituted cinnamic acids (Vyas and Bokil, Rasayanam, 1939, I, *6*, 200; Patel and Bokil, Bomb. Univ. Jour., 1942, X, *5*, 123-27). The failure to get these cinnamic acids in the free condition in these reactions seems to be due partly to the presence of alkoxy group in the benzene nucleus, and partly to the fact that the alkyl group in the β-position facilitates rapid addition of phenol ethers to these cinnamic acids formed as intermediate products in the above reaction, ordinary cinnamic acid, or one substituted only in the benzene nucleus; is not found to add phenol ethers under the same conditions. In this connection the following synthetically prepared substituted β-methylcinnamic acids and esters were found to add, very rapidly, phenol ethers such as anisole, phenetole and orthocresol methyl ether, in the presence of 80% sulphuric acid, producing β-β-disubstituted butyric acids.

(1) ethyl β-methyl cinnamate; (2) ethyl β-p-dimethyl cinnamate; (3) ethyl p-methoxy-β-methyl cinnamate; (4) ethyl p-ethoxy-β-methyl cinnamate; (5) ethyl o-methoxy-β-methyl cinnamate; (6) 6-methoxy-β-3-dimethyl cinnamic acid. The following two acids, which are prepared for the first time, are, however, not found to add phenol ethers under the same conditions, probably due to steric conditions:—(7) β-methyl-β—(1-methoxy—2-naphthyl) acrylic acid; (8) β-methyl-β (2-methoxy-1-naphthyl) acrylic acid. β-phenyl cinnamic acid (Rupe and Busolt, Ber, 1907, *40*, 4539) is also not found to add phenol ethers under these conditions.

The first five cinnamic esters were prepared by the condensation of bromacetic ester with the corresponding substituted acetophenones in presence of zinc, according to the method of Lindenbaum (Ber, 1917, *50*, 1270-73). Most of the required acetophenone derivatives were best prepared by the method described by Noller and Adams (J.A.C.S.

1924, *46*, 1889). Ortho methoxy acetophenone was, however, prepared by methylation of the corresponding hydroxy compound synthesised according to the method of Fries (Ber, 1910, *43*, 115). 6-methoxy β-3-dimethyl cinnamic acid (K. von. Auwers, Annalen, 1917, *413*, 258, 276) was prepared in a nearly quantitative yield by methylation of the corresponding 4-6-dimethyl coumarin by a method similar to one used by Canter and Robertson (J.C.S., 1931, 1875). 4-6-dimethyl coumarin (Dey, J.C.S. 1915, 1636, is now prepared, in a high yield, by condensing acetoacetic ester with p-cresol in presence of 80% sulphuric acid. 4-methyl-1 : 2-α-β-naphthapyrone (m.p. 167 °C, Bartsch, Ber, 1903, *36*, 1966 ; Dey, J.C.S., 1915, 1606) could be more conveniently prepared by condensing acetoacetic ester with α-naphthol in presence of 80% sulphuric acid. Methylation of this, according to the method described above, gave β-methyl-β-(1-methoxy-2-naphthyl) acrylic acid (m.p. 137 °C). Complete demethylation occurs during anilide preparation and condensation with phenol ethers in presence of 80% sulphuric acid.

4-methyl-1 : 2-β-α-naphthapyrone (m.p. 180 °C; Bacovescu, Ber, 1910, *43*, 1280; Dey, *loc. cit.*, 1628; Dey, Rao and Laxminarayanan, J. Ind. Chem. Soc. 1932, 73-75,) has now been prepared by using 80% sulphuric acid as condensing agent. Though the crude yield was considerable, the amount of the pyrone obtained was only 30% (*cf.* Dey and Laxminarayanan, J. Ind. Chem. Soc., 1932, 153-154). An indication of the formation of a stable β-methyl cis-naphtha-coumarilic acid was obtained from the fact that the ether soluble portion gave more of the naphthapyrone (ether insoluble) when kept overnight with concentrated sulphuric acid (blue fluorescence test); it could not, however, be separated in a pure condition. Methylation of the pyrone gave β-methyl-β-(2-methoxy-1-naphthyl) acrylic acid (m.p. 188°—189 °C) which gets demethylated during reactions as mentioned above.

The β-β-disubstituted butyric acids, obtained by the addition of phenol ethers to the above cinnamic acids and esters and their derivatives, are described in the tabular form for the sake of brevity.

EXPERIMENTAL

4-6-dimethyl coumarin:—To a mixture of p-cresol (0.1 mol.) and acetoacetic ester (0.1 mol.), 80% sulphuric acid (80 gms.) was added with stirring, and the mixture allowed to stand for 24 hours. After decomposing with crushed ice (100 gms.), the separated solid was allowed to stand in the acid liquid for two hours for complete disintegration. The solid was shaken with 5% caustic soda solution, filtered, washed and dried —yield was 70% of the theoretical ; recrystallised product melted at 148 °C ; mixed melting point with an authentic sample did not change.

(Found: C=75.3, H=5.8 per cent. Calculated for $C_{11}H_{12}O_2$— C=75.8, H=5.7 per cent.).

6-methoxy-β-3-dimethyl cinnamic acid:—The above coumarin (10 gms.) was suspended in a mixture of methyl alcohol (85 C.C.) and caustic soda solution (85 C.C. of 20%) in a flask fitted with a reflux condenser and heated (water-bath) until dissolved. After cooling to 50 °C, dimethyl sulphate (50 gms.) was gradually added, maintaining the temperature at

90 °C. The contents were then heated for one and a half hours, after which 100 C. C. more of the alkali solution (20%) were added, temperature brought down to 50 °C, and more of dimethyl sulphate (25 gms.) was gradually added. The whole bulk was now heated for two hours to hydrolyse the ester formed. The alkaline solution was cooled, filtered and acidified—yield 10.5 gms., 90% of the theoretical. Thick rhombic plates from alcohol m.p. 123 °—124 °C; mixed with an authentic sample, the m.p. did not change.

(Found: C=69.6, H=6.6 per cent. Equit. wt. =207.6. Calculated for $C_{12}H_{14}O_3$, C=69.9, H=6.79 per cent. Equit. wt. = 206).

4-methyl-1: 2-α-β-naphthapyrone:— α-naphthol (25 gms.) was dissolved in acetoacetic ester (27 gms.), and 80% sulphuric acid (180 gms.) was added in five minutes with shaking. During the addition the mixture turned green and soon a semisolid appeared which increased to a big lumpy mass in the end. The mixture was slightly warmed for a minute, and then kept at the room temperature for 24 hours. On pouring over crushed ice (150 gms.) the separated sticky solid gradually disintegrated into a granular red mass. This was shaken with 5% caustic soda solution, filtered, washed and dried; when washed with cold alcohol, a fine red powder was obtained—yield 31 gms., 85% of the thereoretical. Recrystallised product melted at 167 °C; melting point of the mixture with an authentic sample did not change.

(Found: C=79.4, H=4.8 per cent. Calculated for $C_{14}H_{10}O_2$—C=80.0, H=4.76 per cent.).

B-methyl-β-(1-methoxy-2-naphthyl) acrylic acid:—The above pyrone (8 gms.) was dissolved in a mixture of alcohol (200 C.C.) and 30% caustic soda solution (60 C.C.) by heating (water bath) and methylation was carried out, as described above, with 35 C.C. of dimethyl sulphate. After heating for two hours, 40 C.C. more of the alkali were added and 12 C.C. of dimethyl sulphate were again run in and the whole mixture was heated for two hours for completing the hydrolysis. The alkaline liquid was diluted, filtered and acidified when a thick liquid separated on vigorous shaking and solidified on standing overnight. The ether extract of this was washed with sodium carbonate solution which, on acidification, gave a grayish green semisolid which solidified on standing and stirring—yield 5.5 gms. About 2 gms. of the pyrone was recovered from the ethereal extract. The acid was crystallised from dilute alcohol in the form of clusters of needles, and from benzene in the form of thin long needles—m.p. 137 °C.

(Found: C=74.1, H=6.1 per cent.; Equit. wt.=243.5; $C_{15}H_{14}O_3$ requires C=74.4, H=5.8 per cent.; Equit. wt.=242).

Ethyl ester prepared by the usual Fischer Speier method, distilled between 280°—290° C/9 mm.; $N_D^{30.5}$=1.5815.

(Found: C=75.2, H=6.8 per cent; $C_{17}H_{18}O_3$ requires C=75.55, and H=6.6 per cent.).

Methyl ester, prepared in a similar way, distilled between 280 °—285 ° C/14 mm.; $N_D^{30.5}$=1.5937.

(Found: C=74.7, H=6.4 per cent.; $C_{16}H_{16}O_3$ requires C=75.0, and H=6.25 per cent.).

4-methyl-1: 2-β-α-naphthapyrone:—β-naphthol (8 gms.) was dissolved in acetoacetic ester (10 gms.) with a little warming, and 80% sulphuric acid was added when a white solid separated at once; after warming a little, the mixture was set aside at the ordinary temperature for 24 hours. The mixture was worked up as in the previous case, and the alkali insoluble sticky, shining reddish mass thus obtained (8 gms.)—70% of the theoretical—was taken up in ether in which some whitish powdery mass (1.5 gms.) remained insoluble, giving the characteristic blue fluorescence in concentrated sulphuric acid. The recrystallised product melted at 180°—181°C; mixed with an authentic sample, the melting point did not change.

(Found: C=79.5; H=4.85 per cent. Calculated for $C_{14}H_{10}O_2$ C=80.0; H=4.76 per cent.).

β-methyl-β-(2-methoxy-1-naphthyl) acrylic acid:—The pyrone (7 gms.) was practically dissolved in a boiling mixture of methyl alcohol (200 C.C.) and 20% caustic soda (100 C.C.), and methylated with 30 C.C. dimethyl sulphate as described in a previous case. After boiling for two hours, 50 C.C. of the alkali, and 12 C.C. of dimethyl sulphate were added and again boiled for two hours. After working in the usual way, 3 gms. of the methylated acid were obtained, and 3 gms. of the pyrone were recovered. The acid was crystallised from benzene in the form of fine needles, m.p. 188°—189°C.

(Found: C=74.7; H=5.7 per cent.; Equit. wt.=242.5; $C_{15}H_{14}O_3$ requires C=74.4; H=5.8 per cent.; Equit. wt.=242).

General procedure for the condensation of phenol ethers with the various cinnamic esters and acids:—

The cinnamic esters, or acids, and phenol ethers are mixed together in the molecular proportions, and 80% sulphuric acid—in the proportion of 80 gms. per 0.1 mol. of the reacting materials—is gradually added with shaking and the mixture allowed to stand for 3—4 hours with occasional shaking. It is then decomposed by pouring over crushed ice, and extracted with ether; the ether extract is washed with sodium carbonate solution, then with water, dried, and ether evaporated, giving the ester of the resulting butyric acid. The alkaline extract, on acidification, gave the corresponding butyric acid which, in the crude condition, is either granular solid, semisolid or thick liquid. Ethyl esters—not obtained directly from the condensation reactions, methyl esters and some anilides are also prepared and given in the following table.

Name of the Compound	Formula	m. p., b.p., etc.	Analysis	
			Found	Required
β-phenyl-β-(p-methoxy phenyl) butyric acid	$C_{17}H_{18}C_3$	Starry needles from ligroin, m.p. 100°-102°C.	C=75.1, H=6.8 Eq. wt.=272.2	C=75.5 per cent. H=6.6 ,, ,, 270 ;
Ethyl-ester	$C_{19}H_{22}O_3$	b. p. 210°-217°/12 mm. $D_{4}^{32.5^\circ}$ =1.0910 ; $N_{D}^{32.5^\circ}$ =1.5492	C=76.2 H=7.5	C=76.5 ; ,, ,, H=7.4 ; ,, ,,
Methyl ester	$C_{18}H_{20}O_3$	b. p. 200°-205° C/5 mm. $D_{4}^{31.9^\circ}$ =1.1200 $N_{D}^{31.9^\circ}$ =1.5570	C=76.4 H=6.8	C=76.05 ,, ,, H=7.04 ,, ,,
β-phenyl-β-(p-ethoxy phenyl) butyric acid	$C_{18}H_{20}O$	A thick jelly, b. p. 270°-275° C/20 mm.	C=76.3 H=6.9 Eq. wt=283.1	C=76.05 ,, ,, H=7.04 284 ; ,, ,,
Ethyl ester	$C_{20}H_{24}O$	b. p. 200°-210° C/8 mm. $D_{4}^{32.5^\circ}$ =1.0750, $N_{D}^{32.5}$ =1.5437	C=76.6 H=7.7	C=76.9 ,, ,, H=7.7 ,, ,,
Methyl ester	$C_{19}H_{22}O_3$	b. p. 185°-195° C/7 mm. $D_{4}^{32.5^\circ}$ =1.0920 $N_{D}^{32.5^\circ}$ =1.5502	C=76.2 H=7.6	C=76.5 ,, ,, H=7.4 ,, ,,
β-phenyl-β-(4-methoxy-5-methyl phenyl) butyric acid	$C_{18}H_{20}O_3$	Granules fom dilute alcohol, m.p. 118°C.	C=76.4 H=6.8 Eq. wt=284.2	C=76.05 ,, ,, H=7.04 ,, ,, 284;

Ethyl ester	$C_{20}H_{24}O_3$	b. p. 210°-218° C/14 mm. $N_D^{32.5^\circ}=1.5426$	C=77.3 H=7.6	C=76.9 H=7.7	„ „ „ „
Methyl ester	$C_{19}H_{22}O_3$	b. p. 190°-200° C/8 mm. $N_D^{32.5^\circ}=1.5512$	C=76.8 H=7.2	C=76.5 H=7.8	„ „
β-(p-methyl phenyl)-β-(p-methoxy phenyl) butyric acid	$C_{18}H_{20}O_3$	Small prismatic needles, from dilute alcohol, m.p. 130°C.	C=75.8 H=7.2 Eq. wt.=285.6	C=76.05 H=7.04 284;	„ „ „ „
Ethyl ester	$C_{20}H_{24}O_3$	b.p. 230°-235° C/10 mm. $D_4^{35.5^\circ}=1.0770$; $N_D^{28.3^\circ}=1.5491$	C=76.5 H=7.8	C=76.9 H=7.7	„ „ „ „
Methyl ester	$C_{19}H_{22}O_3$	b. p. 210°-215° C/6 mm. $N_D^{35.1^\circ}=1.5539$	C=76.9 H=7.1	C=76.5 H=7.4	„ „ „ „
β-(p-methyl phenyl)-β-(p-ethoxy phenyl) butyric acid	$C_{19}H_{22}O_3$	First purified by distillation, b.p. 230°-240° C/6 mm.; then crystallised from methyl alcohol and dilute HCl, granules m.p. 112° C.	C=76.2 H=7.5 Eq. wt.=296.1	C=76.5 H=7.4 298;	„ „ „ „
Ethyl ester	$C_{21}H_{26}O_3$	b.p. 220°-228° C/6 mm. $N_D^{28.3^\circ}=1.5432$	C=77.7 H=7.7	C=77.3 H=8.0	„ „ „ „
Methyl ester	$C_{20}H_{24}O_3$	b. p. 210°-220° C/9 mm. $D_4^{32.5^\circ}=1.0760$; $N_D^{29.3^\circ}=1.5486$	C=77.3 H=7.5	C=76.9 H=7.7	„ „ „ „

Name of the Compound	Formula	m.p., b.p., etc.	Analysis	
			Found	Required
β-(p-methyl phenyl)-β-(4-methoxy-5-methyl phenyl)-butyric acid	$C_{19}H_{\;2}O_3$	Small needles from dilute alcohol, m. p. 130°-132°C.	C=76.1 H=7.6 Eq. wt. 298.4	C=76.5 per cent H=7.4 ,, ,, 298; ,, ,,
Ethyl ester	$C_{21}H_{26}O_3$	b. p. 205°-215°C/6 mm. $N_D^{28.5°}=1.5486$	C=76.9 H=8.2	C=77.3 ,, ,, H=8.0 ,, ,,
Methyl ester	$C_{20}H_{24}O_3$	b. p. 220°-225° C/10 mm. $N_D^{28.5°}=1.5510$	C=77.4 H=7.4	C=76.9 ,, ,, H=7.7
Anilide	$C_{25}H_{27}O_2N$	Starry needles from alcohol, m.p. 140°-141°C.	N=3.6	N=3.75 ,, ,,
β-(p-methoxy phenyl)-β-(p-ethoxy phenyl) butyric acid	$C_{19}H_{22}O_4$	Granules from dilute alcohol, m.p. 99°-100.C.	C=72.2 H=7.1 Eq. wt.=312	C=72.6 ,, ,, H=7.0 ,, ,, 314;
Ethyl ester	$C_{21}H_{26}O_4$	b. p. 240°-250°C/11 mm. $D_4^{32.5°}=1.0960$ $N_D^{29.8°}=1.5421$,	C=73.4 H=7.8	C=73.8 ,, ,, H=7.6 ,, ,,
Methyl ester	$C_{20}H_{24}O_4$	b. p. 245°-255° C/9 mm. $N_D^{32.1°}=1.5502$	C=73.6 H=7.2	C=73.2 ,, ,, H=7.3 ,, ,,
β-(p-methoxy phenyl)-β-(4-methoxy-5-methyl phenyl) butyric acid	$C_{19}H_{22}O_4$	Cauliflower crystals from alcohol, m. p. 120°C.	C=72.3 H=7.2 Eq. wt.=316.1	C=72.6 ,, ,, H=7.0 ,, ,, 314;
Ethyl ester	$C_{21}H_{26}O_4$	b. p. 245-250° C/12 mm. $N_D^{29.5°}=1.5521$	C=73.5 H=7.75	C=73.8 ,, ,, H=7.6 ,, ,,
Methyl ester	$C_{20}H_{24}O_4$	b. p. 235°-240° C/ 9 mm. $N_D^{32.1°}=1.5583$	C=73.5 H=7.1	C=73.2 ,, H=7.3 ,, ,,

β-(p-ethoxy phenyl)-β-(4-methoxy-5-methyl phenyl) butyric acid;	$C_{20}H_{24}O_4$	Granules from dilute acetic acid, m.p. 103°-104 C.	C=72.8 H=7.5 Eq. wt.=325.4	C=73.2 „ „ H=7.3 „ „ 328;
Ethyl ester	$C_{22}H_{28}O_4$	b. p. 250°-260° C/ 8 mm. $N_{D}^{33.7^\circ}=1.5463$	C=74.4 H=7.65	C=74.1 „ „ H=7.86 „ „
Methyl ester	$C_{21}H_{26}O_4$	b. p. 245°-250° C/10 mm. $N_{D}^{33^\circ}=1.5528$	C.73.9 H=7.4	C.73=8 „ „ H=7.6 „ „
β-(o-methoxy phenyl)-β-(p-methoxy phenyl) butyric acid	$C_{18}H_{20}O_4$	Rhombic prisms from dilute methyl alcohol, m. p. 118°-119° C,	C=71.8 H=6.8 Eq. wt.=303	C=72.0 „ „ H=6.6 „ „ 300;
Ethyl ester	$C_{20}H_{24}O_4$	b. p. 230°-235° C/10 mm. $N_{D}^{31.3^\circ}=1.5532$	C=73.4 H=7.1	C=73.2 „ „ H=7.3 „ „
β-(6-methoxy-3-methyl phenyl)-β-(p-methoxy phenyl)-butyric acid	$C_{19}H_{22}O_4$	A mixture of acids purified by fractional distillation of methyl ester, and hydrolysis of the first fraction.—Small needles from alcohol, m.p. 158°C.	C=72.2 H=7.2 Eq. wt.=311.7	C=72.6 per cent. H=7.0 „ „ 314;
Methyl ester	$C_{20}H_{24}O_4$	b. p. 240°-250° C/20 mm. solidifies, granules from 80% alcohol, at 0°C.—m.p. 86-87°C.	C=72.9 H=7.4	C=73.2 „ „ H=7.3 „ „
β-(6-methoxy-3-methyl phenyl)-β-(p-ethoxy phenyl)-butyric acid:	$C_{20}H_{24}O_4$	Prismatic needles from alcohol, m.p. 148°C.	C=73.6 H=7.1 Eq. wt.=325.8	C=73.2 „ „ H=7.3 „ „ 328;
Ethyl ester	$C_{22}H_{28}O_4$	b. p. 300°-305° C/6 mm. $N_{D}^{30.5^\circ}=1.5588$; solidifies, granules from 80% alcohol, at 0°C.—m.p. 72°C.	C=73.8 H=8.1	C=74.1 „ „ H=7.86 „ „
Anilide	$C_{26}H_{29}O_3N$	Short needles from alcohol, m.p. 149°C.	N=3.3	N=3.5 „ „

Name of the Compound	Formula	m p., b.p., etc.	Analysis	
			Found	Required
β-(6-methoxy-3-methyl phenyl)-β-(4-methoxy-5-methyl-phenyl) butyric acid	$C_{20}H_{42}O_4$	Prismatic needles from alcohol, m.p. 157°C.	C=72.7 H=7.6 Eq. wt.=326.8	C=73.2 ,, ,, H=7.3 ,, ,, 328;
Ethyl ester	$C_{22}H_{28}O_4$	b. p. 270°-275° C/2 mm. solidifies, flakes from 80% alcohol, at 0°C,—m.p. 84°C.	C=74.5 H=7.7	C=74.1 ,, ,, H=7.86 ,, ,,
Methyl ester	$C_{21}H_{26}O_4$	b. p. 255°-260° C/2 mm., solidifies, granules from alcohol, m.p., 84°-85° C.	C=73.5 H=7.8	C=73.8 ,, ,, H=7.6 ,, ,,
Anilide	$C_{26}H_{26}O_3N$	Starry needles from alcohol, m.p. 144°C.	N=3.55	N=3.47 ,, ,,

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M. R. SCIENCE INSTITUTE,
GUJARAT COLLEGE, AHMEDABAD

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IMPROVED PREPARATION OF 4-NITRORESORCINOL

By

N. B. PAREKH AND R. C. SHAH

4-NITRORESORCINOL has been prepared before by various workers in different ways. It was first isolated by Weselsky along with 2-nitroresorcinol as a secondary product in the preparation of diazoresorcinol, by the action of nitric acid containing nitrous acid on an ether solution of resorcinol (Weselsky, Annalen, 1872, *164*, 1; Weselsky and Benedict, Wien Akad. Ber., (2) *82*, 1219).

A. Fevre (Compt. Rend. 1883, *96*, 790) obtained a mono nitroresorcinol by the action of amyl nitrite on monosodium resorcinol, followed by treatment with sulphuric acid.

By the oxidation of 4-nitrosoresorcinol with hydrogen peroxide in alkaline solution, Borsche and Berkhout (Annalen, 1903, *330*, 106) and Ehrlich (M, *8*, 926) claimed to have obtained 4-nitroresorcinol in 70 per cent. yield.

Schiaparelli, Abelli (G. *13*, 258) and Errera (G. *15*, 272) prepared 4-nitroresorcinol from 4-nitroresorcinol dibenzoate, (prepared by the treatment of resorcinol dibenzoate with nitrosyl sulphuric acid (Schiaparelli, Abelli, B., *16*, 872) by boiling with alcoholic potassium hydroxide.

V. Hemmelmayr (M. *26*, 1905, 185) obtained 4-nitroresorcinol by heating 5-nitro-β-resorcylic acid with water in a sealed tube at 160°.

Kauffmann and Kugel (Ber., 1911, 44, 753) obtained two isomeric nitroderivatives by nitrating resorcinol monobenzoate both of which yielded 4-nitroresorcinol on hydrolysis. (Weselsky, *loc. cit.*).

Baker and Lothian (J. 1936, 280) have referred to the difficulty in preparing 4-nitroresorcinol. They found that 4-nitrosoresorcinol could not be oxidised with hydrogen peroxide under conditions described by Borsche and Berkhout (*loc. cit.*). By the modification of Gilbert, Laxton and Prideaux (J. 1927, 2299), they were however able to obtain a small yield of 0.5 gm. of 4-nitroresorcinol from 10 gm. of the potassium salt of 4-nitrosoresorcinol.

Chakravarti (J. Ind. Chem. Soc., 1937, *14*, 37) has prepared 4-nitroresorcinol by Borsche and Berkhout's method (*loc. cit.*) in spite of the poor yield it provided.

It therefore appeared that no satisfactory method to prepare 4-nitroresorcinol in quantity has so far been devised. Since 4-nitroresorcinol was required in a fairly large amount for synthetic work, the problem of its preparation was independently investigated. The method of Kauffmann and Kugel (*loc. cit.*), was tried and the difficulty was found that resorcinol monobenzoate was obtained in poor yield even after modifications by changing the concentrations. Nitration of β—resorcylic acid according to the directions of Hemmelmayr was carried out at higher temperature, but 5-nitro-β-resorcylic acid obtained along with styphnic acid was found to be in poor yield. In order to improve the yield the nitration of methyl-β-resorcylate was carried out. The product obtained was found to be methyl 5-nitro-β-resorcylate, which on hydrolysis with alkali gave 5-nitro-β-resorcylic acid. The yield then was found to be improved, but only to 27 per cent. With a view to improve the yield still further, the nitration of β-resorcylic acid at room temperature was investigated. By this method 5-nitro-β-resorcylic acid was obtained in 55 per cent. yield without any trace of styphnic acid.

The decarboxylation of 5-nitro-β-resorcylic acid under conditions described by Hemmelmayr (*loc. cit.*) could not be carried out smoothly and the product was obtained in a highly impure state. To improve the yield a large number of exploratory experiments was carried out by heating 5-nitro-β-resorcylic acid in a sealed tube with varying proportions of concentrated hydrochloric acid, glacial acetic acid and water for different intervals of time at various temperatures. The conditions for the smooth decarboxylation of 5-nitro-β-resorcylic acid was finally worked out. By heating 5-nitro-β-resorcylic acid for 10 to 11 hours at 140°-145° with a mixture of one part by volume of glacial acetic acid, one half part by volume of concentrated hydrochloric acid and two and half part by volume of water, 5-nitro-β-resorcylic acid was decarboxylated completely and the solution was obtained of clear orange yellow colour. The melting point of 4-nitroresorcinol was found to be 122° agreeing with that of Kauffmann and Kugel and not 115° as recorded by others.

EXPERIMENTAL

Methyl-β-resorcylate was prepared by Robinson and Shah's method (J. 1934, 1496).

5-nitromethyl-β-resorcylate : Concentrated HNO_3 (d. 1.42, 200 c.c.) was added drop by drop to methyl β-resorcylate (50 g.) kept in a 2 litre beaker. The mass left behind after the vigorous evolution of fumes had ceased, was diluted with water and the solid obtained was washed and crystallised from methyl alcohol (charcoal) in shining yellow needles, m.p. 163°-67° (37 g.).

Hemmelmayr (M. 25, 33, 1904) has obtained the above product from 5-nitro-β-resorcylic acid and methyl alcohol with HCl and recorded m.p. 167°.

Hydrolysis of methyl 5-nitro-β-resorcylate to 5-nitro-β-resorcylic acid.

5-nitro-β-methyl resorcylate (25 g.) was refluxed with NaOH (20%, 200 c.c.) on a water bath for 3 hours. It was then acidified with concentrated HCl. The solid obtained was crystallised from methyl alcohol in fine yellow needles, m.p. 215° (15 g.).

Preparation of 5-nitro-β-resorcylic acid by the improved method.

In a one litre flat bottomed flask β-resorcylic acid (25 g.) was taken and concentrated HNO_3 (d. 1.42, 50 c.c.) was added drop by drop from a dropping funnel. After the evolution of fumes had ceased, the mixture, protected from moisture with a $CaCl_2$ tube, was kept overnight. It was then diluted with water and the solid that separated was washed and crystallised from methyl alcohol in shining yellow needles, m.p. 215° (12.5 g.). V. Hemmelmayr (N. *25*, 21, 1904) prepared the same acid along with styphnic acid by warming β-resorcylic acid with HNO_3 (d. 1.4) and recorded m.p. 167°.

Decarboxylation of 5-nitro-β-resorcylic acid: 4-nitro-resorcinol.

To effect decarboxylation various experiments were carried out. 5-Nitro-β-resorcylic acid was heated alone and with water at temperatures varying from 100° to 200° in oil-baths. In all cases the product was found either in an unaltered state or as a charred mass.

Hemmelmayr's method (*loc. cit.*) of heating the acid with water in a sealed tube at 160°-170° for 7 hours was tried. It was obtained in very poor yield and other methods were therefore thought of and investigated.

5-Nitro-β-resorcylic acid was heated in sealed tubes with varying proportions of acetic acid, HCl and water at different temperatures. At lower temperatures the acid was recovered unaltered and at higher temperatures the product was obtained in uncrystallisable charred state. By repeating the same experiment at 135° and continuing the heating for 10 to 12 hours, half the product was found to be decarboxylated. By heating for ten more hours the substance was found to be completely decarboxylated. By heating 5-Nitro-β-resorcylic acid (5 g.) with acetic acid (10 c.c.), concentrated HCl (15 c.c.) and water (15 c.c.) at 140°-145° for 6 hours in a sealed tube nearly 1/3 of the substance was found to be decarboxylated. Longer heating charred the product. Ultimately the best conditions were found to be the following:—

5-Nitro-β-resorcylic acid (5 g.) was heated in a sealed carius tube with glacial acetic acid (10 c.c.), concentrated HCl (5 c.c.) and water (25 c.c.) for 10 to 11 hours at 140°-145°. The dark yellow solution obtained was extracted with ether and the acetic acid was removed over caustic soda in a vacuum desiccator. It was crystallised from hot water and dried over H_2SO_4 in a vacuum desiccator, m.p. 80°. It was recrystallised from chloroform in needles, m.p. 122° (2.8 g.). It is easily soluble in ether, alcohol benzene and less soluble in chloroform and carbon tetrachloride.

Lit. m.p., P. Weselsky (*loc. cit.*) 115°; A. Fevre (*loc. cit.*) has recorded no definite m.p.; Borsche (*loc. cit.*); 115°; V. Hemmelmayr (*loc. cit.*) 80° and after dehydration 115°; Kauffmann and Kugel (*loc. cit.*) 122°; Baker and Lothian (*loc. cit.*) recorded 115°.

DEPARTMENT OF ORGANIC CHEMISTRY,
ROYAL INSTITUTE OF SCIENCE,
BOMBAY

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SYNTHETICAL ANTHELMINTICS

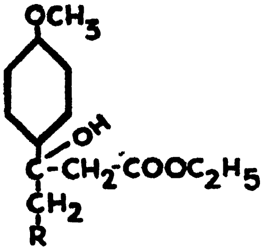
Part VI—β-p-methoxy phenyl-γ-alkyl butyrolactones

By

MISS K. PARANJAPE, N. L. PHALNIKAR AND K. S. NARGUND

γ-p-METHOXY phenyl butyrolactone which was shown to have thrice the anthelmintic properties of santonin by Rosenmond and Schapiro (Arch. Pharm. 1934, *272*, 313) has been taken by Nargund and collaborators as a standard substance and various substituents have been introduced into its structure with a view to correlate the structural changes with those in the anthelmintic properties. The introduction of an alkyl group profoundly modifies the physiological properties of a drug, possibly by increasing its solubility in lipoids. To test the effect of an alkyl group on the anthelmintic properties, various γ-alkyl-γ-p-methoxy phenyl butyrolactones were prepared by Trivedi and Nargund (Jour. Bom. Univ. 1941, *10*, 102). With the same purpose in view β-p-methoxy (hydroxy) phenyl-γ-alkyl butyrolactones are now prepared and described in the present communication.

The method chosen for the preparation of the above-mentioned compounds was the following. The Reformatsky's reaction of ethyl bromoacetate with alkyl p-methoxy phenyl ketones gave β-p-methoxy phenyl-β-hydroxy-γ-alkyl butyrates (I). Dehydration of (I) with phosphorus pentoxide in benzene solution (Kon and Nargund, J. C. S. 1932, 2461) gave ethyl-β-p-methoxy phenyl-γ-alkyl Δ^b butenoates (II), which by cold alkaline hydrolysis gave the corresponding acid (III). The latter on treatment with 60 per cent (wt) sulphuric acid at room temperature for 100 hours was smoothly converted into the lactone (IV). The above procedure for the conversion of βγ-unsaturated acid into butyrolactone was found to be better than the treatment of the unsaturated acid with 60 per cent (vol) sulphuric acid at 90° for 20 minutes—a process described by Linstead and Meade (J.C.S. 1934, 942). Demethylation of the methoxy lactones (IV) by hydrobromic acid in acetic acid gave hydroxy lactones (V).



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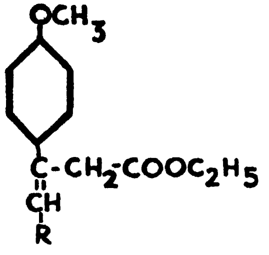

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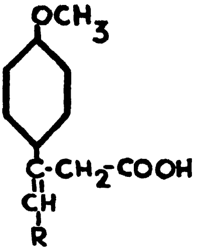

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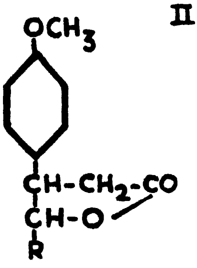
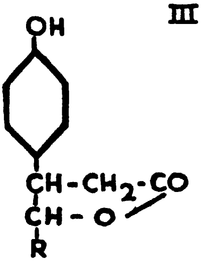


IV



V

Alkyl p-methoxy phenyl ketones required for this work were prepared by Friedel and Craft's reaction of an appropriate acid chloride on anisole using nitrobenzene as solvent (Paranjape, Phalnikar and Nargund, Jour. Bom. Univ. 1942, *11*, 120).

The experimental details are given in case of compounds obtained from p-methoxy phenyl heptadecyl ketone. Similar methods were used in other cases and the compounds described in tabular form.

EXPERIMENTAL

Ethyl β-p-methoxy phenyl β-hydroxy γ-hexadecyl butyrate :—A mixture of p-methoxy phenyl heptadecyl ketone (37.4 gms), zinc (6.5 gms), ethyl bromoacetate (16.9 gms), and toluene (200 cc) was heated on a sand bath. A vigorous reaction ensued at the boiling point of toluene. After two hours boiling it was decomposed with ice and dilute sulphuric acid and toluene removed by steam distillation. The residue crystallised from ethyl alcohol m.p. 60°, yield 70 per cent. (Found: C, 75.0; H, 11.1 per cent. $C_{29}H_{50}O_4$ requires C, 75.3 H, 11.3 per cent).

β-p-methoxy phenyl β-hydroxy γ-hexadecyl butyric acid :—The above ester was boiled with excess of ten per cent alcoholic potassium hydroxide for two hours. After removing the neutral impurities it was acidified and the product recovered. It crystallised from methyl alcohol in plates m.p. 71°. (Found: C, 74.8; H, 10.6 per cent. Eqt. wt, 440.0. $C_{27}H_{46}O_4$ requires C, 74.7; H, 10.6 per cent. Eqt. wt, 434.0).

Ethyl β-p-methoxy phenyl γ-hexadecyl Δ^b butenoate :—A mixture of ethyl β-p-methoxy phenyl β-hydroxy γ-hexadecyl butyrate (4.6 gms), phosphorus pentoxide (1.8 gms) and benzene (20 cc) was heated on water-bath for three hours. It was then decomposed with water and benzene removed by steam distillation. The residue crystallised from ethyl alcohol in small leaflets m.p. 68°, yield 60 per cent. (Found: C, 78.4; H, 10.8 per cent. $C_{29}H_{48}O_3$ requires C, 78.4; H, 10.8 per cent).

β-p-methoxy phenyl γ-hexadecyl Δ^b *butenoic acid* :—A mixture of the above ester and ten per cent alcoholic potassium hydroxide (50 per cent excess) was kept at room temperature for 48 hours. The unhydrolysed ester was removed by ether extraction and the acid recovered by acidification. It crystallised from ethyl alcohol in needles m.p. 76°. (Found: C,77.6; H, 10.7 per cent. Eqt. wt, 420.0. $C_{27}H_{44}O_3$ requires C, 77.9; H, 10.6 per cent. Eqt. wt, 416.0).

β-p-methoxy phenyl γ-hexadecyl γ-butyrolactone :—The above acid (1 gm) was mixed with 60 per cent. wt, sulphuric acid (20 cc) and kept at room temperature for 100 hours. It was then poured in water, extracted with ether. The ether layer was thoroughly washed with a solution of sodium bicarbonate and then with water, dried over calcium chloride and the product recovered. It crystallised from hexane m.p. 58°, yield 90 per cent. (Found: C, 77.9; H, 10.2 per cent. Eqt. wt, by back titration, 417.7. $C_{27}H_{44}O_3$ requires C, 77. 9; H, 10.6 per cent. Eqt. wt, 416).

β-p-hydroxy phenyl γ-hexadecyl γ-butyrolactone :—The above lactone (1 gm) was boiled for three hours with a saturated solution of hydrobromic acid in acetic acid (10 cc). The product recovered crystallised from hexane m.p. 78—79°. (Found: C, 77.5; H, 10.4 per cent. Eqt. wt, by back titration, 402.4. $C_{26}H_{42}O_3$ requires C, 77.6; H, 10.5 per cent. Eqt. wt, 402).

Name of the Compound	Formula	Method of Preparation and Properties	Analysis	
			Found	Required for
Ethyl β-p-methoxy phenyl β-hydroxy hexoate	$C_{15}H_{22}O_4$	By Reformatsky's reaction of ethyl bromoacetate with 4-methoxy butyrophenone, yield 50 per cent, b. p. 155 at 25 mm.	C, 67.7 ; H, 8.3 per cent.	C, 67.6 ; H, 8.3
β-p-methoxy phenyl β-hydroxy hexoic acid	$C_{13}H_{18}O_4$	Alkaline hydrolysis of the above ester, b.p. 168 at 25 mm.	C, 65.4 ; H, 7.6 Eqt. wt, 238.7	C, 65.5 ; H, 7.5 Eqt. wt, 238.
Ethyl β-p-methoxy phenyl Δ^b hexenoate	$C_{15}H_{20}O_3$	By dehydration of the hydroxy ester by phosphorus pentoxide in benzene solution, yield 60 per cent, b.p. 170 at 20 mm.	C, 72.5 ; H, 8.1	C, 72.6 ; H, 8.1
β-p-methoxy phenyl Δ^b hexenoic acid	$C_{13}H_{16}O_3$	By cold alkaline hydrolysis of the above ester, b.p. 210 at 25 mm. gave an anilide m.p. 110.	C, 70.8 ; H, 7.3 Eqt. wt, 219.6	C, 70.9 ; H, 7.3 Eqt. wt, 220
β-p-methoxy phenyl γ-ethyl γ-butyrolactone	$C_{13}H_{16}O_3$	By lactonisation of the above acid by 60 per cent sulphuric acid, b.p. 185 at 20 mm., yield 90 per cent. $D_4^{28} = 1.0110$ $N_D^{28} = 1.47326$	C, 70.9 ; H, 7.3 Eqt. wt by back titration, 220.6	C, 70.9 ; H, 7.3 Eqt. wt, 220
β-p-hydroxy phenyl γ-ethyl γ-butyrolactone	$C_{12}H_{14}O_3$	Demethylation of the above lactone by hydrobromic acid in acetic acid, b.p. 198 at 35 mm. $D_4^{28} = 1.016$ $N_D^{28} = 1.47219$	C, 69.9 ; H, 6.9 Eqt. wt by back titration, 204.6	C, 69.9 ; H, 7.0 Eqt. wt, 206.0
Ethyl β-p-methoxy phenyl β-hydroxy heptoate	$C_{16}H_{24}O_4$	By Reformatsky's reaction of ethyl bromoacetate with p-methoxy valerophenone, b. p. 160 at 25 mm., yield 60 per cent.	C, 68.4 ; H, 8.6	C, 68.6 ; H, 8.6
β-p-methoxy phenyl β-hydroxy heptoic acid	$C_{14}H_{20}O_4$	By alkaline hydrolysis of the above ester, b.p. 190 at 30 mm.	C, 66.5 ; H, 7.9 ; Eqt. wt, 250.6	C, 66.7 ; H, 7.9 Eqt. wt, 252
Ethyl β-p-methoxy phenyl Δ^b heptenoate	$C_{16}H_{22}O_3$	By dehydration of the hydroxy ester by P_2O_5 in benzene, b.p. 170 at 20 mm., yield 60 per cent.	C, 73.1 ; H, 8.4	C, 73.3 ; H, 8.4

Name of the Compound	Formula	Method of Preparation and Properties	Analysis	
			Found	Required for
β-p-methoxy phenyl Δ^{b} heptenoic acid	$C_{14}H_{18}O_3$	By cold alkaline hydrolysis of the above ester, b.p. 195 at 20 mm., gave an anilide m.p. 105.	C, 71.7 ; H, 7.7 Eqt. wt, 234.3	C, 71.8 ; H, 7.7 Eqt. wt. 234
β-p-methoxy phenyl γ-propyl γ-butyrolactone	$C_{14}H_{18}O_3$	By lactonisation of the above acid by 60 per cent sulphuric acid, b. p. 186 at 16 mm.	C, 71.9 ; H, 7.7 Eqt. wt by back titration, 233.4	C, 71.8 ; H, 7.7 Eqt. wt, 234
		$D_4^{28}=1.008$ $N_D^{28}=1.47897$		
β-p-hydroxy phenyl γ-propyl γ-butyrolactone	$C_{13}H_{16}O_3$	By demethylation of the above lactone by hydrobromic acid in acetic acid, b.p. 220 at 35 mm.	C, 70.9 ; H, 7.3 Eqt. wt by back titration, 219 .8	C, 70.9 , H, 7.3 Eqt. wt, 220
		$N_D^{28}=1.47708$		
Hexyl p-methoxy phenyl ketone	$C_{14}H_{20}O_2$	By Friedel and Crafts reaction of heptoyl chloride with anisole. b.p. 240 at 50 mm.	C, 76.1 ; H, 9.1	C, 76.4 ; H, 9.1
		$D_4^{28}=1.007$ $N_D^{28}=1.5114$		
		Yield 70 per cent. Constitution was proved by demethylation to hexyl p-hydroxy phenyl ketone m.p. 94 of Pyman, Marshall and Coulthard (J. C. S. 1930 280).		
Ethyl β-p-methoxy phenyl β-hydroxy nonoate	$C_{18}H_{28}O_4$	By Reformatsky's reaction of the above ketone with ethyl bromoacetate, b p. 220 at 50 mm., yield 50 per cent.	C, 70.1 ; H, 9.1	C, 70.1 ; H, 9.1
		$D_4^{28}=1.060$ $N_D^{28}=1.5124$		
β-p-methoxy phenyl β-hydroxy nonoic acid	$C_{16}H_{24}O_4$	By alkaline hydrolysis of the above ester, b.p. 235 at 45 mm.	C, 68.4 ; H, 8.5 Eqt. wt, 281	C, 68.6 ; H, 8.6 Eqt. wt, 280

Ethyl β-p-methoxy phenyl Δ^b nonenoate (nonylate)	$C_{18}H_{26}O_3$	By dehydration of the hydroxy ester in benzene solution by P_2O_5, b.p. 225 at 45 mm.	C, 74.3 ; H,9.0	C, 74.5 ; H, 9.0
β-p-methoxy phenyl Δ nonenoic acid (nonylic acid)	$C_{16}H_{22}O_3$	By cold alkaline hydrolysis of the above ester, b.p. 240 at 25 mm., gave an anilide m.p. 101.	C, 73.2 ; H, 8.4 Eqt. wt, 261.9	C, 73.3 ; H, 8.4 Eqt. wt. 262
β-p-methoxy phenyl γ-n-amyl butyrolactone	$C_{16}H_{22}O_3$	By lactonisation of the above acid by 60 per cent sulphuric acid, b.p. 245 at 30 mm. D_4^{28}=1.004 N_D^{28}=1.4894	C, 73.4 ; H, 8.4 Eqt. wt, by back titration, 263.1	C, 73.3 ; H, 8.4 Eqt. wt, 262
β-p-hydroxy phenyl γ-n-amyl γ-butyrolactone	$C_{15}H_{20}O_3$	By demethylation of the above lactone by hydrobromic acid in acetic acid. It was a colourless solid crystallising in needles from petroleum ether, m.p. 44.	C, 72.4; H, 8.1 Eqt. wt by back titration, 247.5	C, 72.6 ; H, 8.1 Eqt. wt, 248
Ethyl β-p-methoxy phenyl β-hydroxy octadecylate	$C_{27}H_{46}O_4$	By Reformatsky's reaction of ethyl bromoacetate with p-methoxy phenyl pentadecyl ketone of Paranjape, Phalnikar and Nargund (Jour. Bom. Univ. 1942, *11*, 120), yield 56 per cent. It crystallised in cubes from alcohol m.p. 58.	C, 75.0 ; H, 10.6	C, 74.6 ; H, 10.6
β-p-methoxy phenyl β-hydroxy octadcylic acid	$C_{25}H_{42}O_4$	By alkaline hydrolysis of the above ester. It crystallised in plates from ethyl alcohol m.p. 65.	C, 73.7 ; H, 10.3 Eqt. wt, 404.7	C, 73.9 ; H, 10.3 Eqt. wt, 406
Ethyl β-p-methoxy phenyl Δ^b octadecenoate	$C_{27}H_{44}O_3$	By dehydration of the hydroxy ester by P_2O_5 in benzene solution. It could not be distilled without decomposition and hence not analysed.	Not analysed	

Name of the Compound	Formula	Method of Preparation and Properties	Analysis	
			Found	Required for
β-p-methoxy phenyl Δ^b octadecenoic acid	$C_{25}H_{40}O_3$	By cold alkaline hydrolysis of the above ester. It crystallised in needles from ethyl alcohol m.p. 48. It gave an anilide m. p. 68.	C, 77.2; H, 10.3 Eqt. wt, 387.8	C, 77.3, H.10.3 Eqt. wt, 388
β-p-methoxy phenyl γ-tetradecyl γ-butyrolactone	$C_{25}H_{40}O_3$	By lactonisation of the above acid by 60 per cent sulphuric acid. It was a colourless liquid, b.p. 299 at 25 mm. When cooled in ice it solidified to a solid.	C, 77.3; H, 10.3 Eqt. wt by back titration, 388.8	C, 77.3; H, 10.3 Eqt. wt, 388
β-p-hydroxy phenyl γ-tetradecyl γ-butyrolactone	$C_{24}H_{38}O_3$	By demethylation of the above lactone by HBr in acetic acid. Crystallised in needles from hexane m.p. 45.	C, 77.1; H, 10.2 Eqt. wt by back titration. 374.6	C, 77.2; H, 10.2 Eqt. wt, 374

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MAHARAJA PRATAPSINH CHEMICAL LABORATORY,
SIR PARASHURAMBHAU COLLEGE, POONA

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3-4-DIMETHOXY-PHENYL-SUCCINIC ACID

By

K. P. Dave, J. J. Trivedi and K. S. Nargund

ISOMERIC hydroxy and methoxy phenyl succinic acids have been described before by Dave and Nargund (Jour. Bom. Univ. 1938, *7*, 198, 202). The present work which is a continuation of it describes the synthesis of 3-4-dimethoxy-phenyl-succinic acid.

2-4-dimethoxy phenyl succinic anhydride was the main product of the reaction between maleic anhydride and resorcinol dimethyl ether in presence of anhydrous aluminum chloride (Rice, J.A.C.S. 1931, *53*, 3153). A similar attempt at the condensation of veratrole with maleic anhydride gave only 3-4-dimethoxy-benzoyl-acrylic acid, no trace of the corresponding succinic acid being formed (Dave and Nargund Jour. Bom. Univ. 1938, *7*, 191-195). 3-4-dimethoxy phenyl succinic acid can be very conveniently prepared by Lapworth's method (J.C.S. 1922, *49*, 1699, 2741; *ibid.* 1925, 560). Veratraldehyde on condensation with sodium cyanoacetate gave α-cyano-β-3-4-dimethoxy-phenyl-acrylic acid, the ethyl ester of which readily added on potassium cyanide to yield an oily dicyano ester. The latter on hydrolysis with dilute hydrochloric acid gave 3-4-dimethoxy-phenyl-succinic acid which has been characterised by the usual derivatives.

Experimental

Veratraldehyde was prepared according to the method of Decker and Koch (Ber. 1907, *40*, 4794). Sodium cyano acetate solution was prepared according to the procedure described in Organic Syntheses, Vol.7, page 20.

α-cyano-β-3-4-dimethoxy-phenyl-acrylic acid :—Veratraldehyde (6 gms) sodium cyanoacetate solution (17 cc) and a few drops of ten per cent sodium hydroxide solution were shaken for half an hour at 40°. It was then acidified, filtered and washed; yield 10 gms. It was soluble in alcohol and ethyl acetate, slightly soluble in benzene and insoluble in petrol. It crystallised in yellow feathery needles from hot water m.p. 200°. (Found : C, 61.7; H, 4.9 per cent. Eqt. wt. 230. $C_{12}H_{11}O_4N$ requires C, 61.8; H, 4.7 per cent. Eqt. wt. 233).

Methyl-α-cyano-β-3-4-dimethoxy-phenyl acrylate prepared by Fischer-Speier method was a colourless solid crystallising from methyl alcohol in needles m.p. 122°. (Found: C, 63.0; H, 5.4 per cent. $C_{13}H_{13}O_4N$ requires C, 63.2; H, 5.3 per cent).

Ethyl-α-cyano-β-3-4-dimethoxy-phenyl acrylate prepared similarly crystallised from alcohol in yellow needles m.p. 152°. The same compound was also prepared from veratraldehyde (10 gms) ethyl cyanoacetate (7 gms) and a few drops of piperidine; yield 11.5 gms. (Found: C, 64.1; H, 5.9 per cent. $C_{14}H_{15}O_4N$ requires C, 64.4; H, 5.8 per cent).

3-4-dimethoxy-phenyl-succinic acid :—A mixture of ethyl-α-cyano-β-3-4-dimethoxy-phenyl acrylate (6 gms), potassium cyanide (3 gms) and fifty per cent alcohol (12 cc) was heated on a water bath for two minutes when the ester dissolved. It was then diluted with water and acidified. The reddish oil that separated was extracted with ether and ether removed without drying. Con. hydrochloric acid (5 cc) and water (2 cc) were added to it and boiled for 4 hours. The product obtained was purified by treatment with sodium carbonate solution. It was soluble in hot water, methyl and ethyl alcohol, acetic acid and ethyl acetate but insoluble in petrol. It crystallised from water in pale-yellow flat needles m.p. 130°. Silver, barium and lead salts were insoluble in water. (Found: C. 56.4; H, 6.2. Eqt. wt. 126.2. $C_{12}H_{14}O_6$ requires C, 56.7; H, 5.8; per cent. Eqt. wt. 127).

Methyl-3-4-dimethoxy-phenyl succinate prepared by Fischer-Speier method crystallised from dilute methyl alcohol in long needles m.p. 65°. (Found: C, 59.6; H, 6.5. $C_{14}H_{18}O_6$ requires C, 59.6; H, 6.4 per cent.) Ethyl ester was a gummy substance which could not be purified.

3-4-dimethoxy-phenyl-succinic anhydride prepared from the acid and excess of acetic anhydride on a water bath crystallised from ethyl acetate in prisms m.p. 124°. (Found: C, 59.9; H, 5.4 per cent. $C_{12}H_{12}O_5$ requires C, 61.0; H, 5.1 per cent).

Semianilide of 3-4-dimethoxy-phenyl-succinic acid prepared from the anhydride and aniline in benzene solution crystallised from dilute alcohol in flat needles m.p. 151°. (Found: Eqt. wt. 329. $C_{18}H_{19}O_5N$ requires eqt. wt. 329).

Semi-p-toluidide of 3-4-dimethoxy-phenyl-succinic acid prepared similarly, crystallised from ethyl alcohol in prisms m.p. 158°—159°. (Found: Eqt. wt. 338.4. $C_{19}H_{21}O_5N$ requires eqt. wt. 343).

3-4-dimethoxy-phenyl succinimide prepared by heating the anhydride in a current of dry ammonia crystallised in plates from alcohol m.p. 172° with previous softening at 163°. (Found: N, 6.3 per cent. $C_{12}H_{13}O_4N$ requires N, 6.0 per cent.)

We thank the University of Bombay for a research grant to one of us K. S. N., and the Charak Trust for some chemicals.

M. R. SCIENCE INSTITUTE,
GUJARAT COLLEGE, AHMEDABAD

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The importance of avoiding preventable losses of food grains during storage before its actual consumption should, therefore, be obvious to anyone who is familiar both with the destruction of food grains by weevils and other insects during storage, and the food situation in India during the war. Hence it is very essential to find means of economising the quantity of mercury required for preventing the attack of insect pests, and the loss sustained thereby during the storage. It is reported (Agri. Research Institute, Pusa, *loc. cit.*) that seven ounces of mercury were required to preserve 16 maunds of wheat. (1 maund=80 lbs.). The present price of mercury will act as a deterrent against its use in such quantities as are mentioned in the scientific reports of the Agricultural Research Institute.

Some experiments were therefore undertaken with a view to reduce the quantity of mercury reported to be necessary for the prevention of spoilage of food grains by insects. An account of these experiments together with the observations made in the course of these experiments are presented in this paper. It may be observed here that these experiments were carried out only on a small scale, yet in the light of the results obtained by previous investigators, combined with similar observations in the present experiments of ours, there are very good reasons for believing that the results will be successful on a large scale. We may as well mention here that we are prepared to carry out these experiments under our supervision provided facilities are granted.

EXPERIMENTAL

Instead of using the briquettes of tin mercury amalgam or mercury alone by itself or mercury mixed with cow-dung or soil as was done by previous investigators, we prepared a number of copper sheets measuring 1.5″ long and 1″ broad by coating them with mercury. To coat the copper pieces on both the sides about 0.4 gram of mercury was required. These mercury-coated copper sheets were then kept in perforated paper boxes, so that during handling the mercury would not be rubbed away. In these trials husked rice and husked *Vari* grains (Panicum sp.) already infested with weevils and beetles were used. They contained eggs, caterpillars or grubs of various sizes and full grown weevils and beetles. The quantity of grains taken for the experiment was in lots of 5 lbs. each. Tin boxes provided with lids served for storage. The paper boxes containing the mercury coated sheets were placed in the grains stored in the tin boxes. The lids of the tin boxes were kept closed but loosely except when the lids were occasionally opened for inspection to observe the effect of the mercury-coated sheets on the insects at intervals. A detailed examination of the stored grain and the insect pests was made after two months' storage and the following points were noted: (1) The eggs were not microscopically examined, so the effect of mercury on eggs could not be noted at this juncture: but it would be found in the next experiment. (2) All the small sized caterpillars or grubs (less than ⅛″ in length) were found dead in about a fortnight, *i.e.*, in the fortnight immediately after the addition of the copper sheets coated with mercury. (3) Of the larger sized caterpillars or grubs (more than ⅛″ in length) some were dead but a large percentage remained alive and active even after two months in storage. (4) The full grown weevils and beetles present in the sample were unaffected by the treatment during the course of the experiment, *i.e.*, for two months.

At the end of this period of two months all the different samples of grain, both treated and untreated, were cleaned, and the weevils, beetles and caterpillars or grubs were removed by hand picking, but no attempt was made to search for eggs on the grains or remove them. The eggs if any were present on the grains were left, as they were, quite untouched and unharmed. The cleared grain samples were now kept back in the tin boxes together with the mercury-coated copper sheets, observations at intervals were made as before but no weevils or beetles and caterpillars or grubs could be detected in the samples with the mercury-coated copper sheets. After a period of two months, when the samples were taken out, no weevils, beetles and caterpillars or grubs could be found to have developed in the stored grain after the cleaning process showing very clearly that if any eggs were present on the grain at the time of the cleaning process, they could no longer develop in the samples with mercury-coated copper sheets. The untreated samples which had no mercury-coated sheets kept in them, however, had developed caterpillars or grubs and a few weevils or beetles also.

Consumption of the Stored Grain :—One of the samples of rice taken for this experiment was over one year old before it was exposed to mercury treatment. At the end of the experiment, which took more than four months for completion, the samples were cooked and consumed one by one. There was no change in its taste or odour.

When the experiment was first started the husked panicum grains were about eight months old since husking was done. After the total experimental period of four months these panicum grains were also cooked and consumed on several occasions. The taste and smell did not differ from the normal newly husked grain. The untreated control sample in this particular instance was found to be developing slightly bad odour, which of course may or may not be due to the weevil attack.

DISCUSSION

It is quite clear from the above experiments that the small quantity of mercury spread on thin copper sheets served the same purpose as the large quantity of mercury used either alone by itself or in the form of thin briquettes of tin mercury amalgam used by the previous investigators. (Dutt and Puri, Rep. of the Agri. Inst., etc., *loc. cit.*). The quantity of mercury required in our experiments amounts to about one eighth to one twelfth the quantity required by the earlier investigators.

The previous investigators have already concluded from their experiments that the insecticidal property depends on the vapour developed from mercury kept in the space in which the grain is stored. The mercury vapour prevents the eggs from developing into caterpillars or grubs. This conclusion served as our working hypothesis and we planned our experiments to effect an economy in the quantity of mercury to be used for preventing the damage to stored grain by insects, after considering the various points as mentioned below.

The data on the vapour pressure of mercury at different temperatures indicates that mercury possesses very low vapour pressure at atmospheric temperatures. (Landolt Börnstein, Physikalische-Chemische Tabbellen, 5th edition, pp. 1335).

Temp. C	V.P. in m.m. Mercury	Temp. C	V.P. in m.m. Mercury
16	0.00092	28	0.00254
18	0.00110	30	0.00299
20	0.00131	32	0.00350
22	0.00155	34	0.00410
24	0.00183	36	0.00478
26	0.00216		

The evaporation of mercury therefore at these temperatures is negligible. F. Glaser (Zeit. Electro Chem. 1903, *9*,11) states that the loss per sq.c.m. per hour of electrolytically pure mercury is 0.002 milligram at atmospheric temperatures. Thus the total quantity of mercury lost by evaporation is very small. Similarly, the concentration of mercury vapour at these temperatures is also small. But even this small vapour of mercury appears to be quite sufficient to prevent the development of eggs. At the same time this small quantity of mercury vapour is ineffective towards fully grown caterpillars or grubs or weevils or beetles. This observation has a very high significance inasmuch as we can probably conclude from it that the small quantity of mercury vapour will be equally harmless to human beings and the method can be safely used for domestic use.

In different parts of India the atmospheric temperatures vary from 16°C to 34°C or at the most 36°C. The vapour pressure of mercury in this range of temperatures would be between 0.00092 to 0.00410 m.m. The insecticidal effect will naturally be proportional to the quantity of mercury in the form of mercury vapour present in the atmosphere surrounding the grain. So, if we wish to increase the efficiency of mercury vapour (for the prevention of damage by insect pests) we will have to make it attain the proper concentration evenly and rapidly. Now the vapour pressure of mercury depends solely on the temperature, but recourse to high temperature would not be desirable because an unduly large increase of temperature of the atmosphere around the grain would probably result in the deterioration of the grain and may also cause loss of the power of germination, and hence if we want to utilise the small amount of vapour pressure of mercury (attained at low temperature) to its fullest extent and get the maximum benefit therefrom the only alternative available to us is to make the mercury vapour at low temperatures diffuse very rapidly in the space where the grain is stored. The simplest way of accelerating the diffusion of mercury vapour in a given space consists in increasing the surface of mercury emitting the vapour. This can be done by either of these two methods. (1) The first consists in dividing the total quantity of mercury into as many small fractions and keeping these small fractions at a number of different positions in the storage space (a tin, a room, or a gunny bag) instead of the whole quantity of mercury in one place. (2) Another method of achieving the same object consists in spreading the mercury on a large surface, *e.g.*, by coating thin ribbons like metal sheets with mercury. The small pieces of the metal coated with mercury may then be tied up separately in muslin bags or perforated paper boxes and placed at different place in the grain. The surface of mercury thus exposed with a definite quantity of mercury would be very much greater than if the same quantity of mercury were exposed in the form of tin amalgam discs or briquettes.

In our later experiments which are recently being carried out and which are not described here, we have dispersed mercury in fine droplets and deposited them between two ribbons of porous paper. With these paper ribbons we expect that a still smaller quantity of mercury than that used in the present experiments would be sufficient to prevent the damage of food grains by insects. Theoretically, only a few milligrams of mercury properly dispersed would be sufficient to preserve the grain. After making sufficient allowance for the loss by evaporation, about one gram of mercury per palla of 240 lbs. would suffice. This means that there would be an economy to the extent of approximately 1/50th to 1/75th of the quantity used by previous investigators. It may be noted here that mercury even though finely dispersed is perfectly stable and not oxidised so that its activity remains unimpaired. (C. Barfoed, Jour. prakt. Chem., 2, *38*, 458, 1888).

SUMMARY

Insecticidal property of mercury vapour has been studied and while the observation of its effect on eggs of insects is confirmed it has been definitely observed for the first time that mercury vapour also kills the small sized larvae of the insects attacking the food grains in storage.

Suggestions are made to effect economy in the quantity of mercury to be used and to attain greater efficiency with a comparatively smaller quantity of mercury. Fresh experiments are being carried out to further reduce the quantity of mercury and also to determine the minimum quantity of mercury required for the storage of different food grains without damage by insect pests. Attempts are being made to find some compounds of mercury possessing a higher vapour pressure and yet innocuous to human beings.

I wish to express my thanks to Prof. N. V. Joshi, Professor of Microbiology and Bio-Chemistry, Fergusson College, Poona, for his valuable help during the present investigation.

FERGUSSON COLLEGE,
POONA

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THE INTER-TRAPPEAN BEDS AT UPPARHATTI

By

K. V. KELKAR AND R. B. GUPTE

THE object of this paper is to place on record the results of our study of the inter-trappean rocks at Upparhatti, a village about five miles east-by-south of Gokak (Lat. 16° 10′ N. Long. 74° 53′ E.) in Belgaum District. Newbold[1] had noticed these rocks as early as 1845, but it was Foote who first recognised that they are an inter-trappean lake deposit. A brief description of these rocks and a sketch section showing their succession has been given[2] by the latter author in his "The Geological Features of the S.M.C. and Adjacent Districts" and it may incidentally be remarked that though published as early as 1876, it is yet the best available account of the geology of this tract.

As stated by Foote[3] the beds exposed in a section north of Upparhatti are :—

"4. Quartzite and gneiss shingles of uncertain age.

3. Weathered basaltic trap.

2. Red sandy marl with three or four sandstone partings containing Unio (Deccanensis ?).

1. Decomposing whitish amygdaloidal trap."

Attention will be confined in this article to the "Unio" beds forming series 2 in the table above.

The marl contains up to ten per cent of calcium carbonate in the form of calcite and fine calcareous dust. It is admixed with varying amounts of sand. The sandy portion is composed mainly of crystalline quartz, the other constituents being limonite-coated weathered felspar and a few slightly weathered microcline grains. The colour of the rock varying between red and dark brown is due to the presence of limonite.

The sandstones are more or less calcareous and like the marl, coloured by limonite. They are composed of ill-sorted detrital material and in texture vary between fine and very coarse grades. Much coarser fragments, waterworn pebbles and shingles of quartz, are scattered in the beds.

Quartz is the principal constituent of the sandstones and forms subangular anhedral grains. Weathered limonite-coated felspar grains form a subordinate portion. Microcline is present but as a rule in small amounts. The calcareous matter, amounting to less than five per cent of the rock, is mainly calcite but some of it is cryptocrystalline or fine flour-like.

The rocks are loosely cemented and crumble easily into powder.

THE ACCESSORY CONSTITUENTS

The marl and the sandstones yield a fair quantity of heavy residue, the carbonate-free extract, amounting to between 1.1 and 1.8 per cent by weight. Twenty-five grammes of the powdered coarse sandstones and ten of the finer marl, obtained by quartering of the bulk specimen (400—500 gms. in weight), were used in these determinations. Heavy residues were extracted by means of bromoform by following the usual technique.[4] Two parallel series of extracts had to be obtained: 1) From a neutral, i.e. ordinary water digest, and 2) from a weak HCl digest to get rid of the calcium carbonate and the ferruginous stain.

The minerals composing the heavy residue from the marl and the sandstones are identical and need not be described separately. They are opaque iron ores, pink garnet, epidote, tourmaline, actinolite, kyanite, staurolite, zircon, rutile and apatite. Their relevant characters are stated below.

Fe-ores-Magnetite is absent or nearly so. Haematite is the commonest of the ores and occurs as rounded grains appearing earthy reddish brown by reflected light, or as irregular black plates with a splendent lustre. Occasionally changing into limonite. Ilmenite-black, irregular grains, subangular to rounded; several changing into white leucoxene. *Size of the grains—0.51×0.32 mm.

Garnet—pink to nearly colourless. Form—irregular; rarely euhedral, little or slightly rounded rhombic dodecahedra. Grains subangular to well rounded. A few fractured grains. The surface of worn grains usually smooth but many appearing as if they were covered by minute tubercles or aggregates of curved scales. Size—euhedral 0.2 mm. in diameter; well rounded 0.24 mm. across; irregular and subangular—0.7×0.6 mm.

Epidote—usually green or greenish yellow; a few brownish or colourless. Pleochroism feeble in the greenish grains. Form—irregular grains and laths; usually subangular. Nearly one-fourth of the total number of grains show some rounding. A few well rounded. Rarely euhedral. The elongated flattened plates usually exhibit a compass needle figure due to the emergence of an optic axis. Size—euhedral—0.48×0.13 mm.

Tourmaline—pink, pale brown or greenish brown. Pleochroism intense. As a rule shows little rounding. Fractured prisms usually void of terminal faces. Prism faces vertically striated. Size—prisms 0.35×0.16 mm. Irregular grains—0.48×0.22 mm.

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* The maximum observed sizes stated throughout.

Actinolite—green, pale green or colourless; thicker grains bluish green; feebly pleochroic. Irregularly bounded laths or fibrous aggregates. A few changing to chloritic material or coloured by limonite. Size—laths —0.94 × 0.4 mm.

Kyanite—colourless. Subangular prismatic grains with irregular terminations. Often both the (001) and (010) cleavages seen; such fragments extinguish at nearly 30° with reference to the (010) cleavage and show the emergence of the negative bisectrix of a large optic angle. Size—0.59 × 0.21 mm.

Staurolite—pale yellow to brownish yellow; moderately pleochroic. Form—very irregular. Angular to sub-angular fragments. Size—0.62 × 0.35 mm.

Zircon—colourless to very pale brown. Usually euhedral; prisms terminated by pyramid faces. Usually slightly rounded. A few fractured prisms with pyramids at one end. Rarely coarse, well rounded prisms or ellipsoidal grains. Size—well rounded grains, 0.37 × 0.32 mm. Little rounded prisms, 0.19 × 0.05 mm.

Rutile—Reddish brown. Prisms with pyramidal terminations rounded, and ellipsoidal grains. Size—0.16 × 0.02 mm.

Apatite—colourless and clear. Only well rounded prisms and egg-shaped grains occur. Size—0.21 × 0.19 mm.

PROPORTION OF THE ACCESSORY MINERALS

In all six representative specimens—3 of marl and one from each of the three sandstone partings—were used in determining the frequency of the various accessory minerals. There is some variation in the total amount and the relative proportion of the accessories in these rocks; but as variations occur in both, the marl and the sandstone, and to an equal extent, the rocks cannot be distinguished by means of the proportion of the accessories they contain. By averaging the results obtained from the specimens studied the frequency of the minerals of the inter-trappean deposit as a whole may be expressed by symbolic[5] numbers as follows:—

Fe-ores: 6; Garnet: 5; Epidote: 5; Tourmaline: 4; Actinolite: 4; Kyanite: 4; Staurolite: 3; Zircon: 3; Rutile: 1; Apatite: 1.

SOURCE OF THE SEDIMENT

Almost the whole of the material composing these beds has been derived from pre-trappean rocks, contribution of Deccan trap being little if any. None of the essential minerals of the Deccan trap was detected either in the bulk portion or in the accessories, and the majority of the accessory minerals are such as could not be derived from the trap. The probable sources of the detrital material are the Archaean metamorphic rocks and the Kaladgi sediments. The fairly high proportion of subangular and slightly rounded grains of accessory minerals indicates that the material is in the first cycle of sedimentation and that it was derived directly from some Archaean rocks containing garnet, kyanite, staurolite etc. Little can be said at present regarding the locality of the parent rocks.

FOSSILS

An examination of these beds yielded several fossils in addition to the Unio recorded by Foote[6]. They include several gastropod shells like Physa and Limnea and fragments of the skeleton of a Chelonian. A general account of the forms collected is given below.

Unio-Unio shells are the commonest of the few fossils occurring in the sandstone partings.

Shells inequilateral, oval in outline ; the outline of some slightly wavy, the ventral centre portion curving slightly inwards. Surface ornamented with distinct concentric growth lines. Many shells have a ridge, variable in elevation and extending from the umbones to the extremity of the posterior margin. Umbones distinct and marked with faint, radiating, short ridges. Ventral border smooth. There are two varieties which differ only in their relative thickness—one being gibbose and the other rather compressed. Both equally common. Sizes :

Length—67.8 mm.	Breadth—41 mm.	Thickness— 28.8 mm.
,, 74 mm.	,, 43.8 mm.	,, 19.7 mm.

Physa—P. prinsepii (Sow) normal[7] form and also a new form of the following description : shell oval in outline ; spire short ; aperture almost as long as the last whorl. Total height—53.5 mm. Height of spire—14mm. Diameter of the shell—27 mm.

Paludina—Shell small, with four whorls only ; turbinate ; spire short. Imperforate. Aperture round. Surface marked with faint striæ transverse to the whorls. Height—7.7 mm. Diameter—6.2 mm.

Limnæa—Shell very long and slender. Spire long and pointed. Body whorl longer than the spire. Surface smooth. Resembles L. telankhediensis.[8] Height—19.2 mm. Diameter—4.6 mm.

One more gastropod, presumably the Bulimus of earlier writers,[9] is as common as the gastropods described above. It is a long turreted shell with six whorls. Whorls convex. Apex blunt. Whorls increase gradually in size from the apex. Form cylindrically ovate. Coiling dextral. Aperture entire. Peristome slightly reflected. Height—15.3 mm. Diameter—5.8 mm.

In the Chelonian skeleton discovered as loose isolated fragments the following parts can be recognised : Distal piece of femur ; portions of epi-, ento-, xiphi-, and hypoplastron, and marginal and costal plates.

STRATIGRAPHIC POSITION

These beds are already known to be members[10] of the Lower Inter-trappean group. Occurrence of Physa and the other gasteropods mentioned above is an addition to the proofs available showing the close relation between these beds and the Lower Inter-trappean beds of C.P., Central India etc.

We have to thank Prof. B. S. Gogte and Mr. B. G. Shirole of Zoology Dept. of this College for their help in identifying the parts of the Chelonian skeleton mentioned above.

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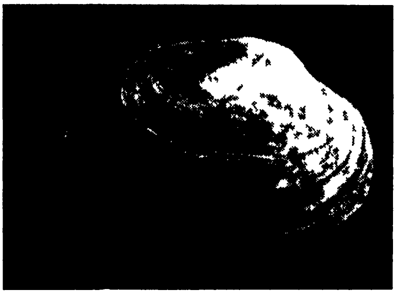
Plate I



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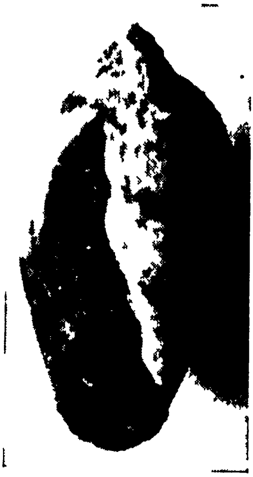

14

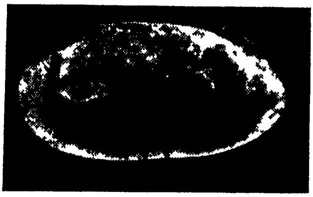

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Plate II

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EXPLANATION OF ILLUSTRATIONS

PLATE I

Nos. I—11. Photomicrographs. Ordinary light. All magnified. 57 ×

1. Garnet—anhedral ; rounded.
1*a*. ,, euhedral ; slightly rounded.
2. ,, rounded. Spotted appearance, the surface tubercular.
3. ,, well rounded ; surface smooth.
4. Epidote—Euhedral ; little rounded.
5. ,, Irregularly bounded lath ; the common form.
6. ,, Rounded grains.
7. Tourmaline—the usual form.
8. Actinolite—the usual form.
9. Kyanite.
10. Staurolite. Anhedral ; little rounding.
11. Zircon. A fractured, slightly rounded grain.

PHOTOGRAPHS

PLATE II

No. 12. . . . . x. Unio. $\frac{7}{1}$ ×
No. 13. . . . . x. Unio. Flattened variety ; right valve. $\frac{9}{10}$ ×
No. 14. . . . . x. Physa, the new variety. Natural size.
No. 15. . . . . x. Paludina. 1½ ×
No. 16. . . . . x. Bulimus, *cf.* page 124 1½ ×

FERGUSSON COLLEGE,
POONA

A STUDY OF DHARWAR ROCKS

Occurring Around Murgod in Belgaum District

By

L. V. AGASHE

THE area studied is situated roughly between longitudes 74° 50′ and 75° 4′ east, and latitudes 15° 49′ and 15° 58′ north. It is very easily approachable from Belgaum; a two hours' journey by motor-bus takes one to Murgod.

Previous work dealing with the geology of this area is found principally in the work published by Foote (Memoir XII, G. S. I. part I). Brief notes on the rocks in this area by Foote also appear in the Belgaum District Gazetteer and at several places in the G. S. I.'s publications. Casual references to rocks in the area have been made even prior to 1857, in papers of Newbold, Christie, and others, and published in "The Geological Papers on Western India" edited by Carter.

Rocks of the Dharwar group occur in the south-west and west in places like Murgod, Rudrapur, Hosur and Bailhongal. They form a part of the main Dharwar band from which the whole system has received its name in Indian geology. Starting from the southern edge of the Deccan trap, this band runs southwards with a width varying from 10 to 16 miles, past Dharwar to the Tungabhadra river, where it spreads out and covers large areas in the Kodur and Shimoga districts of the Mysore State. Rocks under consideration, therefore, form a small part of the northern extremity of the main Dharwar band.

The constituent rocks of the Dharwar band, from Murgod up to Dharwar, are chiefly phyllites, argillites, variously coloured shales, and a few bands of ferruginous quartzites. Some epidiorites occur in the eastern parts of this band, in the neighbourhood of Murgod. (Probably these are the rocks referred to by Foote as contemporaneous traps). A few subordinate bands of calcareous rocks such as calc-actinolite-chlorite schist, banded marble, and chloritic banded marble also occur.

Only a portion of the Dharwar band—the eastern part about 7 miles in width—is included in the area studied. The rocks observed may be arranged as follows in order of importance :—

(1) Epidiorite, green-schist, and a few bands of calc-actinolite-chlorite schist.

(2) Shale, argillite, and chlorite phyllite.

(3) Banded hæmatite quartzite.

(4) Marble and chloritic marble.

A traverse across the remaining portion of the band in the western part showed that it is composed of shales, argillites, chloritic phyllites, and hæmatite quartzites, very similar to those described here. The relative proportion of the rocks shown by the list above only applies to the area studied, and the order will have to be modified if the whole width were taken into consideration. Rocks of group 2 will, then, top the list, and those of group 1 occupy the 2nd place.

A summary of the lithological characters of rocks, and their descriptions are given below.

1. The Epidiorite Group

Rocks of this group occur chiefly in the neighbourhood of Murgod. The portion of the Dharwar band lying adjacent to its junction with granite gneiss, and about four miles and a half in width, is composed chiefly of rocks of this group. Small irregular patches are found further eastwards in the granite gneiss. The group includes the following varieties.

a) Epidiorite.

b) Green schist.

c) Calc-actinolite-chlorite schist.

The Epidiorites :—The epidiorites are dark or dark green in colour and have an aphanitic or a finegrained directionless texture.

Hornblende is the principal constituent of these rocks. It builds minute prisms and needles which are black macroscopically, and have a green colour in thin sections. It is strongly pleochroic in yellow, green, and dark brownish green colours. In addition to the compact variety just described, a fibrous green uralite is also present. It has a paler green colour and shows pleochroism from pale to deep green, or pale green to bluish green colours. The form of the uralite in several places suggests that it is a pseudomorph after pyroxene. In several sections the compact brownish green and the fibrous pale green varieties are closely associated or confusedly intermingled, so that in thin sections a single plate is found to be composed partly of the compact and partly of the fibrous variety.

A little actinolite is occasionally present, but as a rule in very small amounts.

A lime-plagioclase is the principal variety but the composition varies considerably from oligoclase to labradorite. Oligoclase and intermediate andesine are the commoner varieties. When it is sufficiently fresh, it shows polysynthetic twinning on the albite law. Almost everywhere it has weathered yielding epidote, zoisite, clay etc., and only a few fresh grains are noticeable in a slice. The plagioclase has to some extent suffered saussuritisation, and a part of the epidotes has resulted by breaking up of the plagioclase under the conditions of stress.

In addition to the lime plagioclase a little albite occurs in some rocks. It forms colourless, clear, untwinned grains appearing like quartz in thin sections but distinguished by their biaxial figures. The albite has obviously resulted by breaking up of the lime-plagioclase.

A little quartz is present in most of the rocks, and a small amount of biotite occurs in many.

The iron ore is chiefly ilmenite. It is in places little altered, and generally it has changed to a secondary granular sphene (leucoxene) which forms a layer around ilmenite. Pyrites and magnetite are also found occasionally, but are usually subordinate to ilmenite.

Nomenclature :—An epidiorite is defined as a doleritic or basaltic rock in which the augite has suffered alteration to hornblende, so that the rock approaches the composition of a diorite. It is distinguished from diabase by the less extreme alteration of the felspars (*cf.* Holmes—Nomenclature of petrology). The compact or fine textured varieties without foliation have been termed epidiorites. Some of these have a dark green colour in handspecimens, and may also be termed greenstones.

In the earlier stages of dynamothermal metamorphism of basic igneous rocks it is common to find that a number of minerological changes take place at the first onset of pressure before new structures are imposed. At the next stage directed pressure breaks down the original structures, and new parallel structures are set up. Often the distribution of pressure is not quite uniform, and it is a fairly common phenomenon to find foliated and unfoliated varieties in close association.

The bulk of the epidiorites have a compact directionless structure but in a few places they pass into varieties with a faint or a distinct foliation; such varieties have been termed green schists.

The Green schists :—The green schists differ but little from the epidiorites in mineral composition. A compact green hornblende is their chief constituent. The other minerals—lime-plagioclase, epidotes, iron ores, sphene, quartz, and occasionally a little untwinned water-clear albite—are identical with those in the epidiorites described above. Fibrous uralitic amphibole is also occasionally present.

The green schists differ from epidiorites only in having a faint or a distinct schistosity, and their texture is occasionally a bit coarser. Such schistose rocks, however, do not possess any large dimensions. They form only small bands interbedded with the epidiorite, or patches and lenses grading into it. It is often found that the bulk of a band of a massive epidiorite encloses small patches which have assumed the characters of a green schist.

Under the conditions of dynamothermal metamorphism the pyroxene in basic rocks is changed to amphibole ; the lime-plagioclase breaks up into albite and epidotes and other lime-silicates. Typical hornblende schists thus resulting are composed principally of hornblende with bladed and fibrous forms, exhibiting in thin sections various shades of green. The albite appears in bands entirely composed of a mosaic of untwinned water-clear granules resembling quartz. Epidotes and sphene are usually present, and some quartz may also occur.

Such typical schists do not occur ; the lime-plagioclase is chiefly present, and water-clear untwinned albite is absent or occurs in traces. It appears that the green schists and epidiorites represent original basic rocks which have been modified slightly by dynamothermal metamorphism. The pyroxene has been changed to hornblende and uralite; some leucoxene and sphene have been formed from the titaniferous ore. The bulk of the rock remained massive *i.e.*, without a banded structure. But locally where the pressure has been a bit more severe a schistose structure has developed. The lime-plagioclase has not, however, been broken down completely into albite and epidotes.

Doleritic rocks which have been modified by orogenic forces in which the lime-soda-felspar is little altered, the augite has been converted into hornblende, ilmenite, and titaniferous ore into sphene and rutile, and which have more or less distinct schistosity, have been termed schistose amphibolites by Rosenbusch.

The rocks termed green schists, here, belong to the category of "schistose amphibolites" referred to above, and rocks of this type have also been termed "schistose epidiorites" or "diabase schists."

Calc-actinolite-chlorite schist:—A few bands composed of chlorite, actinolite, and calcite are interbedded with the epidiorites and schists mentioned above. The rocks are dark green or green coloured, and have a texture varying between compact and finegrained. They usually possess a distinct schistose structure ; but varieties with a faint or no foliation also occur.

In addition to the three principal constituents mentioned above the rocks contain varying but usually small amounts of quartz, epidote, zoisite, hornblende, ilmenite, leucoxene, pyrites, and magnetite.

The calcite in these rocks occasionally tends to collect into lenticles and streaks which are distributed either parallel to the banding or in an irregular manner. The material composing these patches and lenticles has a saccharoidal texture, and in hand-specimens or in thin sections closely resembles marbles.

2. The Argillite Group

Rocks of this group occur chiefly in the tract between Hosur and Bailhongal. A few beds are also found interbedded with epidiorites at Murgod. They are the principal variety found in the western portion of the Dharwar band.

The common rock type is a finely laminated shale with either a pure white or a grey colour, or coloured variously—yellow, brown, or purple—by ferruginous matter.

The rocks are composed chiefly of the material of clay grade. Owing to their extremely finegrained character it is very difficult to identify with certainty all of the constituent minerals.

A microscopic examination shows that the rocks consist, to a considerable portion, of an extremely fine textured mixture of chloritic scales, weathered turbid grains presumably of felspar, and granules of quartz. In the ferruginous varieties the turbid granules are stained red by limonite.

By washing the powdered rock and separating with the aid of bromoform, tourmaline, zircon, and pyrites were the accessories obtained.

Some of the clay rocks are not so clearly laminated, and are more compact; they have been termed argillites. In the field all gradations are found to exist between shales and argillites, and chloritic phyllites.

The phyllites are finegrained lustrous schistose rocks composed of finely divided quartz and abundant sericitic and chloritic material, and it is the two latter that control the foliation of the rocks. Tourmaline is a common accessory constitutent of some of the phyllites. A little carbonaceous matter occurs in several others.

3. BANDED HAEMATITE-QUARTZITES

These are quite unimportant; only a few bands occur in the neighbourhood of Bailhongal forming conspicuous ridges among the softer chlorite-phyllites, argillites, and shales. As observed by Foote "They are poor in iron, and but rarely show much of the red staining, though frequently jaspideous in texture."

The rocks are composed of micro-and crypto-crystalline silica, and very fine granular ferruginous matter, hæmatite in fresh and limonite in weathered specimens. Portions rich in silica alternate with those rich in ferruginous matter producing parallel bands. The individual bands are as a rule thin, seldom exceeding one or two cms. in width. The bands run fairly straight or are slightly wavy, and only rarely contorted. Ferruginous portions are dark brown or deep reddish brown, and siliceous portions white, grey, bluish, pale brown, or yellowish in colour. The accessories occasionally observed are tourmaline and zircon; no actinolite or cummingtonite etc., were noticed in any of the specimens examined.

4. MARBLES AND CHLORITIC MARBLES

These form only a few narrow bands interbedded with the phyllite or epidiorites. The exposures are so few, and most [illegible] bands so narrow in width that they are likely to escape notice altogether.

Beds of crystalline limestones were noticed at two localities only, in the Hire Budnur nullah and near Bailhongal. A band was also noticed in a nullah near Sanikop, just outside the area studied.

Two types of crystalline limestone occur, *viz.*, (1) Cleaved marble consisting chiefly of calcite, and containing subordinate amounts of quartz, muscovite, chlorite, zircon, apatite, and tourmaline. The rock is distinctly banded. (2) Chloritic marble composed chiefly of calcite, chlorite, quartz, and accessories like pyrites, tourmaline, and zircon. This variety is also distinctly banded, the banding being made still more conspicuous by the parallel grouping of chlorite flakes.

Structure :—The longer directions of calcite grains are more or less parallel, and the disposition of the chloritic and micaceous flakes, and the distribution of quartz grains in streaks emphasize the banded character. The rock resembles the "Gestreckter Koerniger Kalk" described by Rosenbusch (page 556).

Chemical and micro-chemical tests show that the rock is composed entirely of calcite, and that no dolomite is present. The whole of the calcareous material was stained deep blue when Heeger's test was carried out.

FIELD RELATIONS

The portion of the Dharwar band studied is bound on the south-east by a massive granite-gneiss which is composed chiefly of quartz, oligoclase, microcline, biotite and hornblende. An inlier of this gneiss also occurs east of Murgod near Katharigad. The Dharwars and the granite-gneiss are traversed by numerous acid intrusions such as quartz veins, pegmatites, and small granitic intrusions.

The granite-gneiss is also intruded by dolerite dykes.

All these are covered by Kaladgi sediments which occur in the east and north-east of the Dharwar band described above.

Deccan trap is the youngest formation in the area. A portion rests on the Kaladgis in the north-east, and its major part covers the Dharwars in the north and north-west.

As regards the relation of Dharwars with the granite-gneiss, here, something more need be said.

Till comparatively recent times the Dharwars were considered to be younger than the associated gneisses and gneissose granites, and the latter were, in part at least, believed to represent the first-formed crust of the earth. But observation during the last forty years has shown that there are few, if any, rocks which can be regarded as decidedly older than the Dharwars, and that so far as at least Southern India is concerned, the Dharwars are the older rocks and the associated gneissic rocks are younger, and wherever suitable exposures are available the latter exhibit distinct intrusive relationship with the Dharwars.

Turning to the area under consideration it remains to be seen whether any evidences showing a similar relationship are available. Under ideal conditions one would look for evidence of the following character to show that a certain rock mass is intrusive :—

1) Elongation of the intrusive mass (bathylith) parallel to the tectonic axis of the adjacent rocks, and the bathylith itself or its offshoots cutting across the invaded rocks.

2) Evidences that the mass of the bathylith has absorbed or assimilated the invaded formation.

3) Pegmatitic bodies belonging to the same series as the main intrusive body intruding the adjoining rocks and producing pneumatolitic changes in them.

The area studied and mapped being so small it would not be possible to prove that the granite-gneiss forms a batholith intruding the Dharwars. No remarkable minerological changes were observed in any of the epidiorites and schistose epidiorites, either from portion adjacent to the granite-gneiss or from patches resting over or enclosed by it, and no satisfactory evidences proving the assimilation by the granite-gneiss were noticed.

There is some evidence showing the intrusive nature of the granite-gneiss, *viz.*, the presence of a large number of granitic and pegmatitic intrusions into the Dharwars. These occur chiefly in the form of veins which traverse the intruded rocks irregularly. The veins are small in size ; their thickness hardly exceeds a foot or two, and they can be traced for short distances only, at the most a hundred feet. The rocks also occur as dykes and sheets of a comparatively small size, rarely exceeding ten ft. in width and fifty yds. in length.

A number of these intrusions are found crossing the granite-gneiss, and they also abound in the eastern parts of the Dharwar band, *i.e.*, in the portion adjacent to the granite-gneiss. Excellent exposures are available in the Chilar nullah, about a mile west of Murgod. More than a hundred of them can be counted in that locality.

Granitic and pegmatitic intrusions were not found in the western portion of the part of the Dharwar band considered here. They are confined to the eastern parts of the Dharwars, about four miles and a half in width *i.e.*, within a distance of nearly four and a half miles from the junction of the Dharwar and the granite-gneiss.

The largest of the granitic intrusions observed occurs in the Chilar nullah mentioned above; it occurs as a sheet in the Dharwars running parallel to their strike for a little over a furlong ; the width is about fifty feet. There is a close parallelism in mineral composition between such granitic intrusions and the granite-gneiss.

The acid intrusions, like the granite gneiss, have been affected by stress, and exhibit cataclastic phenomena though to a lesser degree.

FIELD STRUCTURES

The rocks occur in the form of distinct beds, and all, except the marbles, continue for long distances, and maintain a fairly uniform thickness. Probably the same remarks apply in the case of marbles, but owing to their small size and the presence of thick soil in these parts, which obscures the underlying rocks, they could be traced for short distances only.

For the convenience of description only the Dharwars have been divided into different lithological groups. They form, however, a conformable series, and no break is perceptible between the different members.

The rocks have been folded, and the structure is mainly synclinal. There is a subsidiary fold, a local anticline, just west of Bailhongal. The axis of folding runs in a N. by W. direction in this area. (The trend changes slightly when the band is traced southward into Dharwar district and Mysore territory). The beds usually show high dips, and in places they have become vertical.

In the north the Dharwars disappear under the Kaladgis and the Deccan trap, both of which rest over them unconformably. In the east they are bounded by a granite gneiss.

THE KIND, DEGREE, AND SOURCE OF METAMORPHISM

The synclinal structure of the Dharwars and their high dips are obviously connected with the orogenic earth-movement which affected the Peninsula at the close of the Dharwar era. Not only have the rocks been folded but several metamorphic changes have also been produced in them. An examination of the lithological characters of the rocks shows, however, that the metamorphic changes have not been very severe, but are of comparatively low grade.

The principal constituents of rocks of the epidiorite group are hornblende, uralite, actinolite, epidote, zoisite, quartz, calcite, and plagioclase. The plagioclase is chiefly lime-plagioclase, but a little water-clear untwinned albite is also present.

Calcite is the principal constituent of the crystalline limestones; calcite, quartz, and chlorite make up the bulk of the chloritic marbles.

In the banded ferruginous quartzites the iron ore is hæmatite, and none of the specimens examined contained amphiboles like actinolite or cummingtonite.

Majority of the minerals mentioned above are characteristic of a low grade of metamorphism, and belong to rocks of epizone of Grubenmann.

Of the remaining rocks chloritic phyllites alone can strictly be referred to the metamorphic division. The shales and argillites have been more or less compacted, and some sericitic and chloritic material must have developed in them under the influence of stress; but they do not show signs of any pronounced alterations, and would normally not be classed with metamorphic rocks at all, unless the term metamorphism is used in a very wide sense. At the most they may be regarded as showing the lowest degree of dynamic metamorphism.

The chloritic phyllites are made up of finely divided quartz, sericitic and chloritic material indicating obviously the rocks of epizone.

The highest degree of metamorphism attained by rocks in this area is to be observed in the epidiorites and green-schists. These are composed mainly of amphiboles like hornblende, uralite, actinolite, and subordinate amounts of epidotes, quartz, lime-plagioclase, albite, iron-ores, and sphene.

It is well known that the characteristic transformation of pyroxenes in simple, *i.e.*, low grade dynamic metamorphism is not uralitisation but chloritisation, and minerals like hornblende and biotite also break down yielding chlorite. The epidiorites and green schists obviously indicate a slightly higher degree of metamorphism than the associated chloritic rocks. But their lithological characters show that they also belong to the epizone, and indicate, on the whole, a low grade of metamorphism. They are to be regarded as cataclastic igneous rocks showing only the initial stages of dynamothermal metamorphism.

To sum up, the rocks forming the Dharwar band in this part show only a low grade of metamorphism in which the stress has been the chief factor. As a result of stress parallel structures have been set up in rocks like the banded marbles, phyllites, and green schists. There has been a little compacting of the clay rocks into argillites. Obviously a certain amount of recrystallisation and new mineral formation has taken place, such as the production of amphibole, sphene, epidote etc. in epidiorites, sericitic and cloritic material in phyllites. But the mineral assemblage on the whole indicates a low grade of metamorphism, mostly that of the epizone. At the most the epidiorites and green schists which are composed of, essentially, hornblende, and not chlorite, may belong to the very early stages in the mesozone.

A considerable portion of the land consisting of the argillites and shales shows little metamorphic alteration.

ORIGIN

The Argillite group :—Argillites and shales form a prominent portion of this group. An examination of fifteen specimens of these rocks shows that they differ little from sedimentary argillaceous rocks in mineral composition. Heavy residues obtained by washing the powdered rock did not exhibit any minerals that would suggest that the rocks had attained any high grade of metamorphism, or that they are the products of weathering of some highly metamorphosed rocks. In their bedding and lamination they are identical with ordinary mudstones and shales, and the rocks are obviously ordinary argillaceous sediments. They have little altered, and there is nothing to show that their alteration went beyond hardening these rocks a little, and converting them into argillites. The lithological characters of the associated chloritic phyllites show that they have resulted from rocks of argillaceous composition.

Hæmatite-quartzites :—Nothing is to be added regarding the origin of the banded hæmatite-quartzites except that they are now generally regarded to be of sedimentary origin, though the exact mode of sedimentation is not yet fully understood (Presidential addresses, Ind. Sc. Congress 1935 and 1936).

Crystalline limestones :—All the crystalline limestones are banded, and their banding corresponds with the banding of the adjacent rocks. It is obvious that they were calcareous in composition prior to the alteration of the Dharwar rocks by orogenic forces. They might have been either calcareous sediments or material of metasomatic replacement before their being modified by stress. However, here, there is no doubt about their being originally limestone beds of ordinary sedimentary type, for the reasons given below :—

(1) They occur as distinct beds sharply marked off from rocks with which they are interbedded, and do not occur as irregular patches and lenses ; nor do they show any intermediate stages of alteration and gradation into the adjacent rocks.

(2) They maintain their thickness, and have a fairly uniform composition as far as they could be traced. (In the Hira Hullah, a nullah S. W. of Chik-Budnur, a bed nearly 125 ft. thick could be traced for 2½ furlongs till it disappeared under the soil).

(3) They contain accessories like zircon and tourmaline which are absent in the epidiorites with which they are interbedded.

Hence the rocks could not have resulted by replacement of the adjacent rocks, but detrital material must have been present in the original rock.

Epidiorites :—The mineral composition of the rocks clearly shows that they have been derived from basic igneous rocks, lavas and sills, under the conditions of dynamic metamorphism. While the bulk of the rocks is composed of massive epidiorites, more or less schistose varieties have been produced when the stress happened to be a little more rigorous.

The calc-actinolite-chlorite schists, which contain quartz, epidote and some hornblende also, obviously represent material derived from the waste of basic igneous rocks containing detrital quartz, or weathered basic rocks and their tuffs.

CHEMICAL CRITERIA

Inferences regarding the origin of the Dharwar rocks, stated in the preceding paragraphs, have been drawn mainly from the mineral composition, the structure, and the field characters of the rocks. These inferences are in general corroborated by their chemical characters.

A summary of the chemical criteria applied in determining the origin of the metamorphic rocks has been given by Holmes in his "Petrographic methods and calculations." The criteria are :—(1) The proportion of the residual alumina, or the corundum of the norm ; (2) The relative proportions of potash and soda ; (3) The relative proportions of lime and magnesia ; and (4) The amount of residual silica or quartz of the norm.

Excess of alumina, potash exceeding soda, magnesia more than lime, and very great excess of quartz of the norm favour the derivation of a metamorphic rock from detrital sediment.

Attention may now be turned to the argillaceous group first. Results of quantitative chemical analyses of two typical and fresh specimens from the area, are given in table No. 1. An inspection of their chemical composition shows that the rocks are characterised by a very great excess of alumina, and by abundance of silica. Potash much exceeds soda. The rocks are on the whole poor in lime and magnesia ; the lime and magnesia either equal in amount or the lime slightly exceeds the magnesia. That means three out of the four criteria favour the sedimentary origin.

The amounts required to satisfy the ratio of alumina to soda, potash, and lime, in the rocks, is 5.11 in the shale and 4.99 in the phyllite, while the residual alumina or the corundum of the norm amounts to 17.34 and 5.81 respectively. The amount of potash in both the rocks exceeds that of soda by 3.4 in the shale, and 2.1 in phyllite. Lime in both the cases exceeds the magnesia by 0.42 in shale and 0.01 in phyllite. A calculation of the norm shows that the shale contains 49.62% of quartz and the phyllite 61.44%.

The characters have been summarised in table No. 2.

There is no difficulty in connection with the parentage of the banded marbles. They are made up chiefly of calcite, the amounts of the norm in the two specimens analysed being 73·9 and 45·7%. Their calcareous nature, combined with their structure and field characters, shows that they have been derived from calcareous sediments. Their chemical composition is given in table No. 3.

The chemical criteria favour the derivation of green schists from basic igneous rocks. The specimen analysed shows a considerable excess of lime over magnesia, and of soda over potash (CaO 12.16%; MgO 4.62%; excess of CaO 7.54); (Na_2O 1.48%; K_2O 0.25%; excess of Na_2O 1.23). The quartz of the norm amounts to 4.38 % only. There is no corundum in the norm. The chemical composition and the norm of the rock is given in table No. 4.

TABLE I

Chemical Analyses

Rock	Shale	Phyllite
SiO_2	65.55	77.46
Al_2O_3	22.45	10.80
Fe_2O_3	3.90	3.92
FeO	Trace	0.23
MgO	0.13	0.52
CaO	0.55	0.53
Na_2O	0.18	0.63
K_2O	3.58	2.73
H_2O	4.13	2.10
Carbonaceous matter	*nil.*	1.43
Total	100.47	100.35

TABLE II

Chemical Characters	Shale	Phyllite
Excess of K_2O over Na_2O ..	3.4 (3.58—0.18)	2.1 (2.73—0.63)
Excess of CaO over MgO .	0.42 (0.55—0.13)	0.01 (0.53—0.52)
Combined Alumina ..	5.11	4.99
Corundum of norm ..	17.34	5.81
Quartz of norm ..	49.62	61.44

TABLE III

Chemical Analyses

Rock	Banded Marble	Chloritic Banded Marble
SiO_2	13.52	33.80
Al_2O_3	6.84	8.58
*Fe_2O_3	0.20	4.20
CaO	43.39	29.21
MgO	2.01	1.97
CO_2	32.42	20.13
H_2O	1.82	2.28
Total	100.20	100.17

* Total iron determined as Fe_2O_3.

TABLE IV

Green schist

Chemical Composition		Norm	
SiO_2	48.73	Orthoclase	1.67
Al_2O_3	21.10	Albite	12.58
Fe_2O_3	2.08	Anorthite	50.04
FeO	7.23	Diopside	8.63
MgO	4.62	Hypersthene	15.70
CaO	12.16	Ilmenite	3.65
Na_2O	1.48	Magnetite	3.02
K_2O	0.25	Quartz	4.38
TiO_2	1.92	Water	0.91
H_2O	0.91		
Total	100.48	Total	100 58

FERGUSSON COLLEGE,
POONA

NOTES AND NEWS

A Diagnosis of the Present Situation

THE present conflict in the world and the consequent dire threat to civilization are due to fundamental maladjustments which arise from a lack of perception of the true values of life. The present menace to society is due to a lop-sided development of human nature. Man's ethical and spiritual progress has not gone on side by side with his intellectual progress. The sciences of life have not made as rapid a progress as those of matter. The present troubles are due to our ignorance of man as a whole. We have laid undue emphasis on bread and butter studies, on economics and politics and on physical sciences and ignored biological and sociological sciences, and psychological and cultural studies, with the result that our present civilization has become commercial and shows many ugly and vulgar characteristics. First things are not put first as they should be put in the proper ordering of society.

The present age is a mind-dominated age, in which the lower, concrete mind has become the ruler in man, and the spirit is practically dethroned from the constitution of man, who is supposed to be primarily body and mind, or rather body and brain.

Now the characteristics of the lower concrete mind are self-interest, grabbing for oneself, demanding of rights, separativeness, exclusiveness, intolerance, impatience with the weakness of others, domination, exploitation, profiteering, aggressiveness, use of force, etc. Politicians, statesmen, administrators, educationists, industrialists, and people in general have based their policies and their conduct on this wrong and incomplete concept of man, with the logical consequence that we have competition and wars. The present civilization has, more or less, turned out to be a failure. Two terrible world wars during a short space of twenty-five years with all their implications are the best proofs of it, if any proof is needed. Modern civilization has grown up at random without due consideration of the true nature of man. It has not been built up with due consideration to the best interests of humanity.

Modern civilization is characterized by hurry, rush, bustle, noise, stress and strain. In it few men have time to think on the deeper problems of life. It has made man more superficial than deep. In it man has sunk into indifference to almost everything except money. If the development of human personality is the ultimate goal of our civilization, then so far it has failed, for it has created an environment which is not suitable to the growth and development of the finer qualities of man. "Modern business organization and mass production are incompatible with the full development of the human self," says Dr. Alexis Carrel, the Nobel Prizeman, in his famous book "*Man the Unknown.*" He further says : "Modern civilization has brought about "complete destruction of our ancestral qualities by the idleness, corruption and softness of life." Modern civilization has made everything easy for most of us and we wish to have maximum of pleasure with the minimum of effort ; it has made us more or less effeminate. "Nervous disorders, intellectual weakness and mental deterioration have become more frequent" (Alexis Carrel). Modern Civilization "seems to be incapable of producing people endowed with imagination, intelligence and courage. There is, in practically every country, a decrease in the intellectual and moral calibre of those who are responsible for public affairs and administration. Modern civilization has failed in developing men of sufficient intelligence and audacity to guide it along the dangerous road on which it is stumbling" (Alexis Carrel, "*Man the Unknown*").

It is high time that the Universities of the world and of our country in particular should so orient themselves as to be in a position to supply expert physicians whose duty would be to correctly diagnose the malady from which humanity is suffering at present and suggest adequate remedies for the cure of the same.

D. D. KANGA

CORRECTIONS

In the November 1942 issue of this Journal, Vol. XI, Part 3, on :—

PAGE 114 : The formulæ printed should be taken on page 117 and read in connection with the paper on the reduction of—CH(OH) CCI3 group.

PAGE 117 : The formulæ printed should be on page 114 and read along with the "Aluminium Chloride, a new . . . .etc." paper.

BOOKS RECEIVED

Annual Administration Report of the Civil Veterinary Department, United Provinces, for the year 1941-42.

Annual Report of the Indian Lac Research Institute, Bihar, for the year 1941-42.

Binary Systems—Studies in—,by Miss Nagamani Shama Rao and S. K. Kulkarni-Jatkar. Reprinted from the Journal of the Indian Institute of Science, Vol. 24A, Part III, 1942.

Montana School of Mines—Forty-Second Catalogue of—for 1941-42.

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University of Mysore—Special Public Lectures on the Research Work carried out by members of the staff during 1939-40.

Acknowledgments

Advancement of Science

British Machine Tool Engineering

Bulletin of the Calcutta Mathematical Society

Bulletin of the Indian Industrial Research Institute

Bulletin of the Indian Lac Research Institute

Ceylon Journal of Science—Section A

D. J. Sind College Miscellany of the Faculty of Science

Hindustan Aircraft Gazette

Indian Aviation

Indian Journal of Physics

Transactions of the Institute of Marine Engineers

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Professor of Agriculture which post the author held throughout the full period of investigation. He was assisted by Messrs P. S. Pandya and N.R. Bhat during the first two years of the work and by the junior author till it was completed. The authors therefore take this opportunity to express their thanks to them.

INTRODUCTION

Results of every decennial census reveal a steady increase of population which has to be maintained on the limited amount of land available in the country. To relieve such a situation to a perceptible extent, it is essential that the productive capacity of land should rise to a substantially higher level. Out of the various means of increasing soil productivity, according to *Scientific American*, Supplement No. 2245, dated the 11th January 1919 (page 26), the most important gain is attained by the direct addition of fertilisers to the soil. Although land possesses a large store of plantfoods, the amount which can be available to plants from time to time has been reduced by continuous cropping over centuries without their adequate addition for what maximum possible crops would demand. It must be borne in mind that other methods of increasing the yield such as better tillage and adoption of heavier yielding strains of seed are likely to deplete the soil fertility in course of time by the larger quantity of plantfoods which would be removed by the increased yields. Therefore even with the adoption of other means of increasing agricultural production, a judicious and extended use of manures has long been recognised in the cultural practices of all the civilised countries of the world and scientific investigations are in rapid progress in this direction.

Low Productivity of Indian Soils

Mollison (1900) accepted it as certain that under the existing conditions a great deal of land under cultivation in the Bombay Presidency and especially in the Deccan is undergoing a slow system of exhaustion. Norris R. V. (1920) after a study of the present conditions of Indian soils and the crop yields obtained therefrom remarked that the results of investigations have tended on all sides to demonstrate that a very serious impoverishment of these soils is taking place and that energetic steps are necessary to remedy such a state of affairs. The Review of Agricultural Operations in India for 1925—26 expressed that though much of the land in India is naturally fertile, the soil over large areas has been impoverished as a result of its being cropped year after year without manure. The Review of Agricultural Operations in India for 1927—28 further observes "were it not for the recuperative effects of natural processes in the soil which are fortunately well pronounced in the tropical and subtropical regions, Indian soils would not be producing even the comparatively poor crops they are doing today."

That the productivity of Indian soils is lower than that of some other countries is shown by the information in Table 1 extracted from Commercial India (1931).

TABLE I

Yield per acre in pounds of some of the staple crops in different countries

Name of the crop	India	Japan	Egypt	Great Britain	Canada	U.S.A.
Wheat ..	605	1526	1530	2202	1246	..
Rice ..	1295	3040	2783	..	..	..
Cotton (lint) ..	87	181	371	..	..	158
Sugar-cane (white sugar) ..	2400	3340	3378	(Java) 11988	(Hawaii) 18799	..

It is needless further to labour the point that the manurial requirements of Indian agriculture should receive careful attention of every one concerned with agriculture.

INADEQUACY OF INDIAN MANURES AND NECESSITY OF INVESTIGATING NEW ONES

According to the Review of Agricultural Operations in India for 1926—27, "the average quantity of nitrogen used per acre by all the crops grown in India is probably somewhere in the neighbourhood of 25 pounds." "On this basis," the Review continues, "257 million acres cropped in India would require approximately 6,425,000,000 lbs. of nitrogen." The total output of cattle dung would only amount to 2,175 million pounds nitrogen calculated on the basis of 18 pounds nitrogen per adult head and 4½ pounds nitrogen per head of young stock for their number during the year 1930—31 in British India. It may be estimated that other natural sources such as cattle urine, night soil, sheep and goat excreta, oil cakes, fish manure, bones and other waste products of agriculture such as stalks, groundnut and rice husk, sugarcane trash and weeds could only add 2,850 million pounds of nitrogen. It is, however, to be noted that even all the above available resources of manures are not judiciously made use of. A very large proportion of cattle dung obtainable is used as fuel. As estimated by the above referred to Review, something like 1,600 million pounds of nitrogen is lost in the wasteful practice of burning cattle dung as fuel which cannot be prevented unless the *ryots* could be provided with an equally good and cheap fuel under the existing conditions. Appreciable amount of nitrogen is lost in the process of converting dung into manure. Cattle urine is practically all wasted. The use of night soil and poudrette is yet only restricted to the vicinity of a few large cities and, on account of prejudice, has not been taken up to any perceptible extent in rural areas. According to the above Review of Agricultural Operations in India, "if the export of oil-seeds and oil-cakes were to be prohibited and if all the oil-seeds were to be crushed and the oil-cakes derived therefrom used as manure, the total quantity of nitrogen available from that source would be about 110 million pounds only or 1.7 percent approximately of the total quantity required to produce normal crops."

It will thus be realised that the deficiency even in the ordinary manurial requirements of India is so large that new sources of manures have got to be investigated. The scope for growing green manure crops is but very little on account of short seasons of rainfall. Artificial fertilisers can therefore be counted as a promising source. This class of manures has some advantages over the bulky manures on account of easy and quick availability to the crop, concentrated nature and consequent easy and cheap portability and the possibility of their manufacture to any required extent.

THE SCOPE OF ARTIFICIAL FERTILISERS

The utility of artificial fertilisers was first established at Rothamsted about 90 years ago and since that time the scientific and commercial aspects of the fertiliser industry are rapidly developing.

The local agricultural conditions in India set some limitations on their use. According to Viswa Nath (1932) the average carbon content of Indian soils is 0.6 percent while it ought to be at least 1 percent in order that all the nitrogen content of such soils can be effective. This indicates beyond doubt the necessity of increasing the supply of organic matter to the Indian soils which can only be accomplished by the addition of some form of carbonaceous substances. "For the soils tested," he continues, "neither chemical fertilisers nor organic manures are adequate and it is only by the combination of both that the best results are obtained, organic manures assisting the assimilation of chemical fertilisers." Kleberger (1926) also reports similar results for European soils.

Besides the comparatively low content of organic matter in Indian soils, other conditions such as deficiency of water supply, insufficient content of potash and phosphoric acid in some soils which do not consequently respond to the addition of fertilisers, absence of sufficient margin of profit due to heavy initial cost of fertilisers and transport charges to distant interior places, are others of limiting factors.

There is ample evidence to show that the addition of fertilisers is capable of increasing the yields where the above limitations do not exist or can be overcome.

ARTIFICIAL FERTILISERS FOR INDIAN SOILS

It is a common knowledge now that out of the several elements removed by plants from soil, nitrogen, phosphorous, potassium and lime are generally the ones which require special addition on the part of man because (1) they are removed in comparatively large amounts from the soil by the crops andthe deficiency thus brought inhibits plant growth and (2) they are more likely to be run short by other avenues of loss than by plants.

The methods of soil analysis so far known can only indicate the total quantities of these elements of plant food and whether they are generally sufficient or deficient; but the analytical methods have not yet developed to the extent to say what proportion of plant foods present in the soil are in a form available to various plants.

IMPORTANCE OF NITROGENOUS FERTILISERS

Of the three or four elements of plant-food, the most limiting one is most often nitrogen. The supply of available nitrogen in the soil determines largely the extent of the plant growth and the ability of the crop to avail itself of the other elements. The well-known fact established by innumerable investigations in all the parts of the world that nitrogen is subject to substantial losses from soils by leaching and volatilisation, perhaps more so than any other element, is a further reason for comparatively higher importance of nitrogen. In India with an average nitrogen content of 0.05 percent (Vishwa Nath 1932) as against 0.1 percent of rich soils (Sahasrabudhdhe 1929), the question of nitrogen deficiency becomes all the more emphasised.

It is the realisation of this unique and unquestionable importance of nitrogen to Indian agriculture that has been the genesis of the investigation reported in this publication.

PRESENT POSITION OF NITROGENOUS FERTILISERS IN INDIA

"Up till 1924, India had neglected to make use of the new economic sources of nitrogen," remarks the Fertiliser, Feeding-stuffs and Farm supplies Journal, London 1930. "That year India mnufactured 12,000 tons of ammonium sulphate as a bye-product of steel and other works, but exported it mainly to Java where this fertiliser contributed to the production of cheap sugar which imported into India, entered into competition with the home grown sugar obtained by less scientific methods." Fortunately the position has changed since then and the use of artificial fertilisers has steadily extended during the last few years, till, principally due to the general economic depression, it received a setback in 1930. This will be clear from the figures in Table II reproduced from the Review of Agricultural Operations in India for 1929—30 and 1930-31.

TABLE II

Quantities (in tons) of different kinds of nitrogenous fertilisers consumed in India from 1926 to 1930

Name of the fertiliser	1926	1927	1928	1929	1930
Sulphate of ammonia ..	12935	13610	33065	40940	31190
Nitrate of soda ..	6070	7458	8840	11722	4329
Ammonium phosphate types	3181	4939	3657	3090	2874

Even the largest quantity used is only an insignificant fraction of the huge requirements (page 3) of the vast areas of agricultural land in India.

MANURIAL PROBLEM OF THE DECCAN

The manurial problem of the Deccan is not much different from that of the whole of India just discussed. On the contrary it is here more intensified. According to the Statistical Atlas of the Bombay Presidency 1925, Deccan, next to Sind, has the largest proportion of canal irrigated lands in the Bombay Presidency which grows several important money crops for which practically the whole supply of locally available farm-yard manure is used up and people have been well disposed towards the use of concentrated manures including artificial fertilisers. The dry crops on account of their vast areas have hardly a cartload of farmyard manure to their share annually per acre and the rainfall conditions are not favourable for growing green manure crops. It was therefore thought desirable to investigate whether artificial fertilisers can be useful under these circumstances.

OBJECT OF THIS INVESTIGATION

The foregoing considerations have led to the adoption of the object of the investigation to be to study the effect of the commonly available nitrogenous fertilisers on the staple crops of the Deccan.

REVIEW OF THE PREVIOUS FERTILISER EXPERIMENTS IN THE DECCAN

Increasing use of artificial fertilisers in the Western countries led the Department of Agriculture of the Bombay Presidency to take up some experiments on artificial fertilisers since early in this century. But the experimental technique had not then developed to the same extent as at present and the experiments conducted previous to the year 1928—29 were laid out on the basis of a single plot or at the most two plots per treatment ; the plans did not always provide for a comparison of a single variant ; the period of experiments was not sufficiently long to verify the validity of results, and the factor of soil heterogeneity was not taken into account. The results (*Vide Experiments in Manuring Crops in the Bombay Presidency, 1896—1931*, by D. L. Sahasrabuddhe, Agricultural Chemist to the Government of Bombay) as they go however indicated as follows:—

Amongst the fertilisers tried, sulphate of ammonia was predominant. It was found useful for rice at Alibag, Karjat, Kumpta and Ratnagiri and for sugarcane at Arbhavi, Baramati, Kopergaon and Manjri ; it did not prove advantageous to cotton at Dhulia, Dharwar and Jalgaon, to wheat at Dhulia and *shalu jowar* at Manjri and Dharwar. Nitrate of soda, the next important fertiliser, has been found to be of advantage to sugarcane at Kopergaon and Manjri (but not as good as sulphate of ammonia) and oranges at Modibag (Agricultural College, Poona) ; it however failed to show any advantage to cotton at Arbhavi, Dharwar and Jalgaon. Ammophos gave good results with rice at Kumpta and with sugarcane at Arbhavi but could not show any benefit to cotton at Arbhavi, Dharwar and Jalgaon. Calcium cyanamide was found useful for rice at Kumpta but could show no advantage to cotton at Arbhavi and Dharwar. In respect of non-nitrogenous kinds of fertilisers, sulphate of potash showed advantage to chillies and tobacco but not to other crops ; superphosphate and rockphosphate showed in casual trial an advantage to rice but was not found to be of any use to *jowar* and cotton at Dharwar, to chillies at Dhulia and sugarcane at Manjri.

It would thus appear that the information available on the use of nitrogenous fertilisers as a factor in augmenting crop production in the Deccan was but scanty and of a very fragmentary and uncertain nature.

METHODS AND MATERIALS

It has been generally recognised that in assessing the behaviour of a fertiliser from a pot experiment, information of only a preliminary character can be had. For example, if a crop is found not to respond to a given fertiliser in pot cultures, it may be inferred that the fertiliser under test is likely to be of no use in the field having the type of soil experimented with in the pots; if, on the other hand, a fertiliser is found beneficial in pots, it does not necessarily mean that the same order of results would be obtained in the field as the conditions prevailing in the pots and the fields are vastly different. To obtain results of practical value, therefore, it is essential to carry out the experiments under normal field conditions. The present experiments were accordingly laid and carried out under field conditions from November 1928 to March 1934.

THE LOCALITY SELECTED FOR THE EXPERIMENTS

The Agricultural College Farm at Poona, where the soil, climate and all other environmental conditions are fairly representative of those of the Deccan in general, was selected. This farm is situated on the N.W. side of Poona city on the Ganeshkhind road, having 18°30' north latitude and 73°50' east longitude and an elevation of about 1850 feet above the sea level. The soils of the farm, as of the whole Bombay Deccan, are derived from the Deccan trap and vary from light *murmad* to medium black, the depth ranging from one foot to three feet or more. The farm had been under the control of the college authorities from 1907 and the previous history of the various fields was known ; this was very useful particularly with fertiliser experiments in which residual effects might exercise considerable influence. The lands were fairly level and regularly plotted. All facilities necessary for field experiments of this nature were thus fully available.

The rainfall and temperatures ranged during the period of investigation of six years as follows :

Season	Temperature		Rainfall
	Max.	Min.	Inches
Dry Summer (March—June)	94—109	46—80	0.3— 8
Rainy Season (June—Oct.)	76— 95	56—76	18—27
Winter Season (Nov.—Feb.)	77—101	41—66	.02— 2

A graphical comparison of quarter-monthly distribution of these factors for three out of the six years is set out in figures 1, 2 and 3.

CROPS SELECTED

The scope of the investigation had been restricted to such of the principal crops of the Bombay Deccan for which the Agricultural College Farm conditions were suitable. Sugarcane and rice had been omitted from the present investigation in view of the large amount of work already done and then being done in a systematic manner with these crops on Manjri and Karjat farms by the Bombay Department of Agriculture; moreover Poona is not a typical rice or cotton growing region. These investigations therefore included besides *bajri* (Pennisetum typhoideum) *shalu jowar* (Andropogon sorghum) both of which form important rainfed food-crops of the cereal class, chillies (Capsicum *frutescens*) a partially irrigated or rainfed common spice crop, groundnut (*Arachis hypogea*) a valuable leguminous rainfed oil-seed crop, and onion (*Allium cepa*) an irrigated vegetable crop of the poor as well as the rich. Thus crops grown under almost all the conditions such as rainfed or irrigated, those grown on light, medium and heavy soils and those growing in *kharif* as well as *rabi* season were selected. As the investigation commenced rather late in the year 1928—29, only the two winter crops of *shalu jowar* and onions could be taken up that year.

FERTILISERS SELECTED

The selection of the nitrogenous fertilisers was done keeping in view the commonly available forms. The fertilisers selected with their average composition are given below .—

Name of the fertiliser		*Percentage content of*		
		Nitrogen	*Phosphoric acid*	*Potash*
Sulphate of ammonia	.. ..	20	..	..
Nitrate of soda ..	.. ..	15	..	..
Calcium cyanamide	.. ..	18	..	..
Ammophos ..	.. ..	17	17	..
Leunaphos ..	.. ..	19	17	..
Nicifos ..	.. ..	18	18	..
Nitrophoska tried in	1928—29..	17	19	21
	1929—30..	13	13	11
Complete fertiliser	.. ..	13	13	11

The first year (1928—29) did not include nicifos and complete fertiliser. Ammophos, which is similar in composition to leunaphos, was omitted since the year 1929—30. In the year 1930 leunaphos and nitrophoska were withdrawn from the market by the firms manufacturing them and therefore they were replaced respectively by nicifos and complete fertiliser having identical composition. Complete fertiliser used was made up of a mixture of sulphate of ammonia, bone super phosphate and sulphate of potash supplying nitrogen, phosphoric acid and potash in the same proportion as done by nitrophoska used in the year 1929—30.

RATE OF APPLICATION OF FERTILISERS

This was empirically fixed at such quantities as were thought to be likely to pay according to the values of the present yields of the different crops and in consideration of the observation that cereals are generally nitrogen thrifty crops (Keeble, 1932) i.e., their appetite for nitrogen being satisfied with small quantities. Thus the amounts of nitrogen decided to be applied at the outset were as mentioned below :—

	Pounds of nitrogen per acre
Bajri	10
Shalu jowar	10
Groundnut	20
Chillies	20
Onions	20

After getting a few years' experience with these quantities it was thought desirable to also try double the above quantities in the case of *bajri, shalu jowar* and onions.

METHOD AND TIME OF APPLYING FERTILISERS

The fertilisers were either evenly broadcasted by hand or were drilled, depending on the time and depth of application. In the case of crops which received water on the soil after planting either from rain or from irrigation, they were applied as a top-dressing between lines of a crop about two or three weeks after sowing or planting by spreading them after dilution with fine dry soil to about three times the weight of fertiliser. The material was then well mixed into the soil by stirring. In the case of *shalu jowar* which has generally to grow on conserved soil moisture in rainless winter months, fertilisers were drilled in lines about three inches deep and four and half inches apart by a country drill about two to three weeks before sowing so that the fertilisers may get a chance to get well dissolved by the N. E. showers which are generally received in September and October ; in the year 1928—29 however, the fertilisers were drilled about three weeks after sowing.

BASIC OR FOUNDATION DOSE OF ORGANIC MATTER

The use of fertilisers without any organic matter was considered to be unsound from the present knowledge of the subject (Hutchinson, 1927; Kleberger, 1926 ; Russell, 1920 ; Vishwanath, 1932) and therefore the association of a small amount of farmyard manure with them was provided to furnish the foundation of organic matter. This farmyard manure was given about a month or two before sowing.

SELECTION OF LAND

Fields having soil suitable to the different crops to be grown were spotted, their previous history was studied and those with uniform treatments for the preceding three years were selected.

DESCRIPTION OF SOIL

The chemical and mechanical composition of the fields selected was determined by analysing one representative sample of soils of all the replications included in each experiment. As on examination of a number of results of manurial experiments on soils of which the nitrogen contents differ, the effects of the nitrogen addition have not been found to correspond with the nitrogen contents of the soil and as the character and the scope of the investigation were mainly agronomical, these determinations were not carried out separately for each treatment plot and at periodical intervals. The data regarding these determinations, which in all cases were kindly done by the Agricultural Chemist to the Government of Bombay, are presented in Table III. Details about colour and texture of soils are described in Table IV. The depths of soil and contours of levels in the experimental plots are recorded in several figures or descriptive summaries referred to, under the respective crops and years.

MOISTURE CONTENT OF SOIL

Moisture content of soil during the growing period of all the crops except the regularly irrigated crops of onions have also been determined periodically with a view to afford a study of the effects of any differences in this respect from year to year.

TABLE III

Chemical and mechanical composition of soils of the experimental plots

Analysis of a representative sample of soil in plots No.	Stones on original air dry sample	Moisture on fine air dry matter	On oven dry fine matter										
			Loss on ignition	Sand (acid insoluble)	Lime (CaO)	Nitrogen	Phosphoric acid (P205)	Potash (K20)	Coarse sand	Fine sand	Silt	Fine silt	Clay
	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.
1A to 8A	14.8	8.16	8.92	66.66	7.63	0.098	0.057	..	6.71	17.00	26.16	19.07	13.08
9A to 15A	7.75	6.56	8.63	66.10	5.21	0.09	0.095	0.17	7.32	31.99	17.66	18.19	10.17
19A, 20A, 21B & 22B	6.25	6.38	7.30	68.40	2.33	0.08	0.03	0.25	19.23	30.31	20.33	13.37	5.90
22A to 25A	5.90	6.44	9.31	69.98	2.25	0.092	0.097	0.31	3.33	12.13	13.78	19.08	41.34
1B to 8B	9.50	6.32	7.19	60.60	8.97	0.075	0.05	0.20	8.64	31.59	17.49	16.43	9.54
9B to 11B & 7C to 11C	8.61	7.66	7.73	74.97	1.09	0.086	0.068	..	6.23	21.65	35.10	17.80	9.18
12B to 15B and 12C to 15C	4.50	6.58	7.73	70.30	3.36	0.11	0.105	0.165	8.35	31.91	20.33	18.73	10.17
23B to 26B	3.30	3.42	12.80	67.64	1.98	0.134	0.15	0.18	4.67	14.78	34.00	23.50	14.00
6D to 9D	2.50	6.18	7.81	67.50	1.80	0.07	0.13	0.12	5.81	21.81	21.72	23.54	16.59
10D to 15D	4.10	7.52	9.85	74.48	1.06	0.076	0.044	..	5.50	19.29	28.08	21.60	12.42
19D, 20D, 21E and 22E	2.00	7.24	10.65	74.02	5.03	0.072	0.16	0.18	4.19	11.99	17.39	22.70	20.40
23E to 26E	4.00	7.54	10.17	66.07	5.74	0.073	0.18	0.14	3.24	9.90	14.04	27.54	23.22
315, 316, 324 and 325 ..	..	..	..	..	..	..	..	..	3.90	12.46	6.50	31.00	31.00
282, 283, 290 and 291 ..	4.10	5.16	9.41	70.54	2.65	0.057	0.12	0.15	3.77	14.73	22.44	24.99	24.98
298, 299, 306 and 307 ..	5.00	6.02	9.09	73.37	1.30	0.074	0.114	0.27	4.67	12.37	12.72	18.02	42.40
233, 241, 249, 257, 265 and 273.	4.18	7.96	10.51	71.57	2.44	0.103	0.085	..	5.71	17.97	26.16	20.71	14.72
642, 643, 651 and 652 ..	12.50	8.02	10.46	64.18	5.04	0.10	0.20	0.32	7.60	26.75	33.41	9.30	22.94

TABLE IV

Description of the nature of soil in the experimental plots

Plot Nos.	Nature of the soil
1A to 8A	Sandy loam, coarse in texture and light brown in colour. Slightly varies from plot to plot and within the plot also.
9A and 10A	Sandy loam, coarse in texture and light brown in colour.
11A	Western half of this plot is light brown in colour and coarse in texture while the eastern half is a little finer in texture and darker in colour.
12A	Loamy, fairly fine textured and light brown to medium black in colour.
13A and 14A	Loamy, fairly fine textured and slightly dark in colour.
15A .. .	Loamy, fine in texture and dark brown in colour.
19A and 20A	Clay loam, fine in texture and dark brown in colour with slight variations here and there.
22A to 25A	Clay loam, fine in texture and dark in colour.
1B to 4B	Sandy loam, coarse in texture and light brown in colour with slight variations here and there.
5B	Sandy loam, very coarse in texture and very light in colour.
6B and 7B	Sandy loam, fairly fine in texture and light brown in colour.
8B	Sandy loam, coarse in texture and light brown in colour.
9B to 11B	Sandy loam, very coarse in texture and light brown in colour.
12B and 13B	Sandy loam, fairly fine in texture and brown in colour.
14B and 15B .. .	Sandy loam, coarse in texture and light brown in colour.
21B and 22B	Clay loam, fine in texture and dark brown in colour with slight variations here and there.

23B and 24B	Clay loam, fine in texture and dark brown in colour.
25B and 26B	Clay loam, very fine in texture and dark in colour.
7C to 11C	Sandy loam, coarse in texture and brown in colour.
12C	Sandy loam, very coarse in texture and very light in colour.
13C to 15C	Sandy loam, coarse in texture and light brown in colour.
6D to 9D	Clay loam, fine in texture and dark brown in colour with slight variations here and there.
10D to 15D	Clay loam, fine in texture and brown to medium black in colour.
19D and 20D	Loamy, fairy fine in texture and medium black in colour.
21E and 22E	Sandy loam, coarse in texture and light brown in colour.
23E to 25E	Sandy loam, coarse in texture and light brown in colour. Northern part is comparatively coarser in texture and lighter in colour than the rest.
26E	Sandy loam, very coarse in texture and light brown in colour.
315 and 324	Clay loam, very fine in texture and dark in colour.
316 and 325	Clay loam, fine in texture and dark brown in colour.
282 and 290	Loamy, fine in texture and dark brown in colour.
283 and 291	Clay loam, fine in texture and dark in colour.
298, 299, 306 & 307	Clay loam, fine in texture and dark in colour.
233 and 241	Clay loam, fine in texture and dark in colour. Eastern half is better than western half in texture and colour.
249, 257, 265 & 273	Loamy, a little coarse in texture and dark brown in colour. Eastern half is better than western half in texture and colour.
642 and 651	Clay loam, fine in texture and dark brown in colour.
643 and 652	Clay loam, fairly fine in texture and brown in colour.

ROTATIONS

In order to wipe out differences due to any residual effects of fertilisers, other crops were grown without manure or irrigation for the two years following that of experiment. Thus a crop under fertiliser experiment occupied different locations in different years coming in the same place every third year. The crop immediately preceding the one under experiment except in the case of *shalu jowar* was *nilwa* fodder *jowar* unmanured which being a gross feeder was considered capable of wiping out the residual differences, if any, of the previous experimental treatments. *Shalu jowar* was preceded by Khandesh cotton unmanured.

SIZE OF DIMENSIONS OF THE EXPERIMENTAL TREATMENT

The very first idea of testing fertilisers was in pots ; it was however soon thought that the results obtained from pot experiments would diverge much from those under field conditions to which they are to be eventually applied and it was therefore decided to carry out the experiments in small plots. In the year 1928—29 each treatment plot occupied a gross area of 225 square feet formed by 15 ft. × 15 ft. which after allowing border rings, 2.5 feet wide on all the four sides, gave a net experimental area of 100 square feet. From the year 1929—30 onwards the size of each treatment plot was increased to about 2.5 cents of an acre in all cases except a few in which land fit for experiment was limited, and the size was reduced to about 1.25 cents of an acre. The dimensions of the 2.5 cents plots were either 16 ft. × 68 ft. or 9 ft. × 121 ft. after providing a ring of about 2½ ft. along the long and 7 ft. along the short side of each treatment plot. The ring area was harvested separately in all cases and was not taken into account in calculating the results.

LAY-OUT OF THE EXPERIMENT AND STATISTICAL METHODS EMPLOYED

The latest method of experimental technique evolved by Dr. Fisher at Rothamsted was adopted for the purpose of these experiments from the year 1929—30 onwards. The method followed in the year 1928—29 differed slightly from this and is described under that year. Except in a few cases in which 'Latin square arrangement' was possible, the arrangement of 'Randomised blocks' of Dr. Fisher was followed with as many replications as could be provided. Interpretation of results has been done all through according to the principles and illustrations of Fisher's method as explained by Maskell (1929) in his publication 'Survey of Recent Advances in Statistical Methods'. At a later stage when two different quantities of fertilisers were tried, the comparative results of the two quantities of each of the fertilisers were interpreted by Student's method (1908, 1923 and 1926).

OBSERVATIONS NOTED

All the crops were broadly inspected almost every alternate day throughout the growing period and any striking phenomena noticed were recorded in observation books. After full germination, the magnitude of the stand of the crop was estimated by the eye. The further observations were made very critically at fortnightly intervals and consisted of noting the extent of the effect of fertilisers on the general conditions and growth of the crop, the number of leaves per plant, the number of tillers or branches per plant, leaves on main stem and first branch, height, colour, general vigour of the crop, variations in growth of each treatment plot, the effect of deficiency or excess from mycological and entomological troubles and all other relevant observations pertaining to the needs of the crops. At maturity the number of plants in each treatment plot was counted. In harvesting, the rings were first removed and then the net area of each treatment was harvested and kept separately. The produce was dried and prepared into marketable form. Two consecutive weights found to be constant were accepted as final weights. Other data such as the number and weight of different classes of earheads, quality of produce, food values and all other relevant qualities were collected and studied. Crops grown in the years following the experimental treatment were occasionally inspected with a view to marking any striking residual effect of the different fertilisers applied.

RESULTS AND DISCUSSION

The special conditions and results of the Bajri Crop are set out and discussed in this paper, firstly year by year and finally reviewed for all the years taken together.

The kinds of fertilisers experimented with have been named in various tables of results. Quantities tried were such as to supply per acre 10 pounds nitrogen in the first three years and 20 pounds nitrogen in the last three years in addition to 1¼ cart loads of farmyard manure.

This crop was cultivated as a rainfed monsoon crop, *i.e.*, without any irrigation. Preparatory tillage consisted of ploughing with a turnwrest plough to a depth of about seven inches and subsequent three to four harrowings in the fair season preceding sowing. Farmyard manure was spread after ploughing. Sowing was done by a drill in lines one foot apart by about middle of July at a seed rate of about seven pounds per acre. Generally two weedings and interculturings formed the after tillages. Watching of crop was commenced about ten days after general flowering.

The quality of the grain from each plot was judged for colour, size, hardness and uniformity. A representative sample of grain from all the replications of each treatment was examined for food-value by the Agricultural Chemist to the Government of Bombay.

Other conditions which vary from year to year are given under the respective years.

I. 1929-30

POSITION AND DESCRIPTION OF THE LAND

The experiment was conducted on plots 19D, 20D, 21E and 22E, the previous history of which is stated below :—

Year	Number of the plots	Name of the crop	Rain-fed or irrigated	Amount of manure given per acre	Yield per acre in pounds
1926-27 ..	19D to 22E	Misc.crops for Show	....	....	....
1927-28 ..	19D to 22E	Wheat	Rain-fed	Green manuring	941 grain 1876 bhusa
1928-29 ..	19D to 22E	Bajri	Rain-fed	10 carts F.Y.M.	1809 grain 4385 fodder

Fig. 4 shows contours of levels as well as depths of soil up to murum layer and Tables III and IV give further description of soil in other respects.

In Table V are recorded moisture contents of soil in plot No. 20D.

TABLE V

Percentage of moisture contents of soil on oven dry basis

Date	At 0″ to 6″ depth	At 6″ to 12″ depth	At 12″ to 18″ depth
10th July 1929 ..	27.1	25.9	20.4
24th July 1929 ..	24.65	27.4	26.9
7th August 1929 ..	27.7	24.6	25.4
21st August 1929 .	19.7	22.9	20.1
4th September 1929 ..	14.3	16.4	17.5
18th September 1929 ..	40.0	35.9	31.7
2nd October 1929 ..	34.7	36.8	35.6

QUANTITY OF FERTILISERS

Quantities of fertilisers were such as to supply 10 pounds of nitrogen in addition to 1½ cart loads farmyard manure per acre.

ARRANGEMENT OF PLOTS AND NUMBER OF REPLICATIONS

The actual situation of different treatments in each of the four replications provided is shown in Fig. 5.

CULTURAL DETAILS AND PROGRESS OF THE CROP

The preparatory tillage consisted of discing in October 1928 after the removal of the preceding crop, followed by blade harrowing in January 1929 and discings in February, March and April. Farmyard manure was applied on 4th June 1929 and well mixed by subsequent harrowing. Sowing was done on 10th July 1929 with a country drill with a seed rate of seven pounds to an acre. The variety used was 'Akola.' The germination was quite satisfactory and the stand of the crop was about 85 per cent. Fertilisers were applied as a top-dressing on 25th July by broadcasting between the crop lines and mixed thoroughly with the soil by subsequent intercultivation. Flowering commenced from 17th August. The crop suffered on account of drought in August and the first fortnight of September in all the plots. Harvesting was done on 30th September 1929.

RESULTS

The details of the yield are set out in Fig. 5 and Tables VI and VII.

TABLE VI

Yield of bajri grains in pounds per plot of 2.5 cents of an acre

Treatment	Block 19D	Block 20D	Block 21E	Block 22E	Mean of Four Blocks	Percentage Increase over Check
Sulphate of ammonia ..	38.75	26.94	30.50	24.25	30.11	16.9
Nitrate of soda ..	48.50	20.94	23.25	20.50	28.29	9.7
Calcium cyanamide ..	45.06	26.13	37.00	21.38	32.39	25.7
Leunaphos ..	37.25	32.31	37.75	18.50	31.45	22.1
Nitrophoska ..	42.56	25.06	37.81	15.25	30.17	17.1
No fertiliser ..	30.13	25.63	27.38	19.94	25.77	..
Mean of each block ..	40.38	26.17	32.28	19.97	29.70	..

TABLE VII

Yield of dry straw in pounds per plot of 2.5 cents of an acre

Treatment	Block 19D	Block 20D	Block 21E	Block 22E	Mean of Four Blocks	Percentage Increase over Check
Sulphate of ammonia	101.00	84.00	96.00	76.00	89.25	13.9
Nitrate of soda	126.00	80.75	87.75	64.00	89.63	14.4
Calcium cyanamide	120.00	80.00	89.50	63.50	88.25	12.6
Leunaphos	106.00	76.00	92.50	67.00	85.38	8.9
Nitrophoska	120.00	80.00	90.00	66.50	89.13	13.7
No fertiliser	86.50	85.00	78.00	64.00	78.38	..
Mean of the block	109.92	80.96	88.96	66.83	86.67	..

None of the fertilisers is significantly different from the no fertiliser check or from any other fertiliser, both in respect of grain and straw.

The percentage increases in straw are generally smaller than those of grain with the exception of nitrate of soda.

The ratio of the yield of straw to the yield of grain was worked out from the data recorded in Tables VI and VII and is presented in Table VIII.

TABLE VIII

Ratio of the yield of straw to the yield of grain

Treatment	Block 19D	Block 20D	Block 21E	Block 22E	Mean of Four Blocks
Sulphate of ammonia	2.61	3.11	3.15	3.13	3.00
Nitrate of soda	2.60	3.86	3.77	3.12	3.33
Calcium cyanamide	2.66	3.06	2.42	2.97	2.78
Leunaphos	2.85	2.34	2.45	3.62	2.81
Nitrophoska	2.82	3.19	2.38	4.36	3.18
No fertiliser	2 87	3.31	2.85	3.25	3.07
Mean of each block	2.74	3.15	2.86	3.41	3.04

From the above data it is seen that the capacity of vegetative parts to produce grain is the least with nitrate of soda, most with calcium cynanamide and leunaphos and intermediate with the rest.

Judging from periodical observations on the standing crop, sulphate of ammonia, calcium cyanamide and nitrophoska appeared on the whole superior to no fertiliser in most of the replications.

INFLUENCE OF FERTILISERS ON THE QUALITY OF BAJRI GRAINS

The differences in quality were very slight and not enough to affect the market value. The different treatments stood in the order of :—(1) calcium cyanamide, (2) leunaphos, (3) nitrophoska, (4) sulphate of ammonia, (5) no manure and (6) nitrate of soda.

The food-value analysis of the representative Bajri samples is noted in the subjoined table.

Food Constituents in Percentage	Sulphate of Ammonia	Nitrate of Soda	Calcium cyanamide	Leunaphos	Nitrophoska	No fertiliser
Moisture ..	7.82	7.72	7.40	7.92	7.45	7.57
Ether extract ..	5.03	4.81	5.05	5.20	5.40	5.28
Albuminoids* ..	10.25	9.50	8.63	8.56	9.06	10.94
Digestible carbohydrates ..	71.85	73.02	72.34	73.84	71.25	70.91
Woody fibre ..	1.36	0.78	1.00	0.75	1.09	1.07
Ash** ..	3.69	4.17	5.58	3.73	5.75	4.23
containing *Nitrogen ..	1.64	1.52	1.38	1.37	1.45	1.75
**Sand ..	1.71	2.27	3.48	2.11	3.76	2.32

Albuminoids appear to vary in some inverse relation with the yield (Table VI) except in the case of sulphate of ammonia. There appears to be no such relation in the case of woody fibre and ash contents. The woody fibre is however the largest with sulphate of ammonia and least with nitrate of soda and leunaphos. The ash content is highest with calcium cyanamide and complete fertiliser and lowest with sulphate of ammonia and leunaphos.

With a view to study as to how the different fertilisers act and the reasons of differences in their behaviour, data were collected in regard to the soil and the various phases of plant growth.

The means of the different block yields of grain afford a good comparison of the effect of soil. These vary from 19.97 to 40.38, the range of variation being —32 to +36 per cent from the general mean. An examination of individual block variations reveals both in the case of grain and straw that the highest block yields are associated with finer texture and somewhat darker colour (block 19D), and the lowest yields with coarser texture and light brown colour (block 22E). Soils intermediate in texture and colour (blocks 20D and 21E) stand intermediate in texture and colour. Depths greater than one foot do not appear to influence the yields (Fig. 4) with the same texture and colour. Judging from block means of ratios of yields of straw to grain (Table VIII) it is seen that a unit amount of straw has produced less of grain in poorer than in richer soils. It is not possible to interpret the influence of differences in slopes, as they are mixed with those of many other factors.

A study of the number of earheads per plot as recorded in Table IX shows larger number of earheads for nitrate of soda and leunaphos, all others being more or less equal. The number of earheads per unit area do not appear to have any relation with the fertility of soil except perhaps the poorest soil has given the least number.

TABLE IX

Number of earheads per plot of 2.5 cents of an acre

Treatment	Block 19D	Block 20D	Block 21E	Block 22E	Mean of Four Blocks
Sulphate of ammonia ..	2470	3964	4217	3280	3483
Nitrate of soda ..	4572	5078	4726	3788	4541
Calcium cyanamide ..	4801	2969	3525	2145	3360
Leunaphos ..	2460	3682	4389	4712	3811
Nitrophoska ..	4171	2978	2798	2983	3233
No fertiliser ..	3519	3829	3434	3169	3488
Mean of each block ..	3666	3750	3849	3346	3653

Comparing these data (Table IX) with those of the average yield of grain per earhead as recorded in Table X, it is noticed that the yield of grain per earhead is more or less in the inverse proportion to the number of earheads. Increased yield per acre seems to be made up by increasing the weight of the individual earhead over what would have been the case in compensation for the number of earheads per unit area.

TABLE X

Average yield of grain per earhead in tolas

Treatment	Block 19D	Block 20D	Block 21E	Block 22E	Mean of Four Blocks
Sulphate of ammonia ..	0.628	0.272	0.289	0.296	0.371
Nitrate of soda ..	0.370	0.163	0.185	0.241	0.240
Calcium cyanamide ..	0.376	0.352	0.420	0.347	0.374
Leunaphos ..	0.524	0.305	0.394	0.154	0.344
Nitrophoska ..	0.408	0.337	0.469	0.223	0.359
No fertiliser ..	0.297	0.315	0.371	0.252	0.309
Mean of each block ..	0.434	0.291	0.355	0.252	0.333

II. 1930-31

Position and Description of the Land Selected

The experiment was conducted on plots 1B to 8B, the previous history of which is stated below :—

Year	Number of the Plots	Name of the Crop	Rain-fed or Irrigated	Amount of Manure given per Acre	Yield per Acre in Pounds
1927-28	1B to 6B	Bajri	Rain-fed	*Nil*	1450 grain
	7B & 8B	Groundnut	Rain-fed	*Nil*	1154 pods
1928-29	1B to 6B	Groundnut	Rain-fed	10 carts F.Y.M.	1444 pods
	7B & 8B	Nilwa-jowar	Rain-fed	10 carts F.Y.M.	1652 fodder
1929-30	1B to 6B	Bajri	Rain-fed	*Nil*	1206 grain
	7B & 8B	Bajri	Rain-fed	10 carts F.Y.M.	954 grain

The surface of these blocks had a downward slope of about 1-5 per cent from 1 B on the west to 8 B on the east, and of about 1 per cent from south to north of each block. The depth of soil up to the *murum* layer varied from twelve to fifteen inches generally with the exception of 16 to 20 inches of north ends of Blocks Nos. 7 B & 8 B. Tables III and IV give further description of soil in other respects.

In Table XI are recorded moisture contents of soil in plot No. 5B.

Table XI

Percentages of moisture contents of soil on oven dry basis

Date	At 0″ to 6″ depth	At 6″ to 12″ depth	At 12″ to 18″ depth
9th July 1930 ..	25.34	23.15	21.07
23rd July 1930 ..	27.23	28.54	23.76
6th August 1930 ..	22.85	24.38	21.07
20th August 1930 ..	21.07	22.55	20.48
4th September 1930 ..	27.55	28.54	27.93
18th September 1930 ..	24.38	26.58	24.07
2nd October 1930 ..	24.389	26.269	23.76

QUANTITY OF FERTILISERS

Quantities of fertilisers were such as to supply 10 pounds of nitrogen in addition to 1½ cart loads of farmyard manure per acre.

ARRANGEMENT OF PLOTS AND NUMBER OF REPLICATIONS

The actual situation of different treatments in each of the eight replications provided is shown in Table XII.

CULTURAL DETAILS AND PROGRESS OF THE CROP

The preparatory tillage consisted of ploughing in October 1929 after the removal of the preceding crop to a depth of about seven inches by a turn wrest plough followed by discing early in June and blade harrowing in the middle of June and July. Farm yard manure was applied on 27th May 1930 and well mixed by a disc harrow. Sowing was done on 9th July 1930 with a country drill with a seed rate of six pounds per acre. The variety used was 'Akola.' The germination was quite satisfactory and the stand of the crop was about 80 per cent. Fertilisers were applied as a top-dressing on 25th July by broadcasting between the crop lines and mixed thoroughly with the soil by Planet Junior hand hoes. Later on, the crop was intercultivated once by a pair of country bullock hoes early in August and then by a pair of Planet Junior hand hoes in the middle of August. Flowering commenced from 6th August. The crop suffered slightly on account of long drought in August. This year, about 35 per cent of the earheads were either rendered entirely blank or were only partially filled with grains on account of heavy rains on 2nd September and subsequent days which was the time of pollination. It may be noted here that on account of the slightly sloping nature of the land (Fig. 6) almost all the plots suffered from washing in both west to east and south to north directions while the plots having the treatment of complete fertiliser in block 3B, no fertiliser in 4B, sulphate of ammonia in 6B, complete fertiliser in 7B and nitrate of soda in 8B have also slightly suffered from stagnation of water during the days of heavy rains in September. The effect of the fertilisers on the standing crop, whatever could be marked out, began to be distinctly noticed from 16th August, *i.e.*, after three weeks of their applications. The crop passed a healthy life in all other respects and was harvested on 7th to 11th October 1930.

RESULTS

The details of the yield are set out in Fig. 7 and in Tables XII and XIII.

TABLE XII

Yield of Bajri grains in pounds per plot of 2.5 cents of an acre

Treatment	Block 1B	Block 2B	Block 3B	Block 4B	Block ·5B	Block 6B	Block 7B	Block 8B	Mean of Eight Blocks	Percentage Increase over the check.
Sulphate of ammonia	*a*17.13	*c*25.63	*d*22.63	*d*25.13	*a*17.88	*f*31.75	*b*29.88	*e*23.75	24.22	4.94
Nitrate of soda	*b*20.38	*f*29.75	*e*30.00	*c*26.75	*e*19.63	*a*23.88	*e*30.88	*f*25.38	25.83	11.91
Calcium cyanamide	*c*22.13	*a*22.88	*b*25.00	*e*23.81	*f*23.13	*b*20.63	*c*30.25	*c*23.75	23.95	3.73
Nicifos	*d*23.75	*d*21.75	*a*23.38	*b*22.19	*b*17.25	*d*26.88	*f*28.38	*b*25.50	23.64	2.44
Complete fertiliser	*e*26.00	*b*24.38	*f*23.25	*f*24.63	*c*17.75	*c*24.13	*a*29.38	*d*22.38	23.99	3.94
No fertiliser	*f*23.75	*c*22.63	*c*20.88	*a*24.88	*d*16.13	*e*27.00	*d*26.25	*a*23.13	23.08	..
Mean of each block ..	22.19	24.50	24.19	24.90	18.63	25.71	29.17	23.98	24.12	..

Italic letters before the figures under each block indicate the position from west to east.

TABLE XIII

Yield of dry straw in pounds per plot of 2.5 cents of an acre

Treatment	Block 1B	Block 2B	Block 3B	Block 4B	Block 5B	Block 6B	Block 7B	Block 8B	Mean of Eight Blocks	Percentage Increase over the check
Sulphate of ammonia ..	45	49	51	53	48	79	77	55	57.13	14.26
Nitrate of soda ..	50	56	78	65	54	50	63	63	59.87	19.74
Calcium cyanamide ..	55	50	52	50	50	65	68	56	55.75	11.50
Nicifos	51	40	48	52	49	61	75	59	54.37	8.74
Complete fertiliser ..	62	50	60	55	44	62	76	51	57.50	15.00
No fertiliser ..	55	46	40	51	45	66	54	43	50.00	..
Mean of each block ..	53	49	55	54	48	64	69	55	55.77	..

Nitrate of soda alone is significantly better than the no fertiliser check, both in the case of grain and straw.

The percentage increases in straw are higher than those of grain, the divergence being greater in all other fertilisers than nitrate of soda. The increases in straw have generally the same order of merit as grain.

The ratio of the yield of straw to the yield of grain was worked out from the data recorded in Tables XII and XIII and is represented in Table XIV.

TABLE XIV

Ratio of the yield of straw to the yield of grain

Treatment	Block 1B	Block 2B	Block 3B	Block 4B	Block 5B	Block 6B	Block 7B	Block 8B	Mean of 8 Blocks
Sulphate of ammonia	2.62	1.91	2.25	2.10	2.48	2.48	2.37	2.31	2.36
Nitrate of soda	2.45	1.88	2.60	2.40	2.75	2.09	2.05	2.48	2.33
Calcium cyanamide	2.48	2.18	2.03	2.09	2.16	3.15	2.24	2.35	2.34
Nicifos	2.14	1.83	2.05	2.34	2.80	2.26	2.57	2.31	2.28
Complete fertiliser	2.38	2.05	2.58	2.23	2.47	2.56	2.59	2.27	2.39
No fertiliser	2.31	2.03	1.54	2.05	2.79	2.44	2.05	1.85	2.13
Mean of each block	2.40	1.98	2.18	2.20	2.57	2.50	2.31	2.26	2.31

From the above data it is seen that the fertilisers have not been able to increase the yield of grain commensurately with vegetative matter.

Judging from periodical observations on the standing crop, the treatments showed distinct superiority over check in the number of replications stated against each on dates specified below :—

Treatment	Cases of Superiority over Check out of Eight on Dates		
	2-8-30	16-8-30	30-8-30
Sulphate of ammonia ..	....	4	5
Nitrate of soda ..	....	7	7
Calcium cyanamide ..	....	5	7
Nicifos ..	....	3	4
Complete fertiliser ..	....	4	7

Most of the plots which appeared superior to check during the growing period have also given superior final yields of grain and straw.

INFLUENCE OF FERTILISERS ON THE QUALITY OF BAJRI GRAINS

The differences in quality were very slight and not enough to affect the market value. The different treatments stood in the order of :— (1) nicifos, (2) nitrate of soda and calcium cyanamide, (3) sulphate of ammonia, (4) complete fertiliser and (5) no fertiliser.

With a view to studying as to how the different fertilisers act and the reasons of differences in their behaviour, data were collected in regard to the soil and the various phases of plant growth.

The means of different block yields of grain afford a good comparison of the effect of soil. These vary from 18.63 to 29.17 giving thereby a range of variation of —23 to +21 per cent from the general mean. An examination of individual block variations reveals, both in the case of grain and straw, that the highest block yields are associated with finer texture and somewhat darker colour (blocks 7B and 6B), and the lowest yields with coarser texture and light brown colour (block 5B). Soils intermediate in texture and colour (blocks 1B, 2B ,3B, 4B and 8B) stand intermediate in yields. Depths greater than eleven inches do not appear to influence the yields (*Vide* Fig. 6) with the same texture and colour. Judging from block means of ratios of yields of straw to grain (Table XIV) it is seen that a unit amount of straw has produced less of grain in poorer than in richer soils. It is not possible to interpret the influence of differences in slopes, as they are mixed with those of many other factors.

A study of the number of plants per plot as recorded in Table XV shows :

(1) Other conditions remaining the same, the above variations in the number of plants have not caused any consistent difference in the yield per unit area.

(2) The fertilisers have not given any better stand over no fertiliser or between themselves. The varying fertilities of blocks have also not shown any difference in this respect.

TABLE XV

Number of plants per plot of 2.5 cents of an acre

Treatment	Block 1B	Block 2B	Block 3B	Block 4B	Block 5B	Block 6B	Block 7B	Block 8B	Mean of 8 Blocks
Sulphate of ammonia	2000	1536	1568	1323	1678	1818	1795	1932	1706
Nitrate of soda	1658	1763	1490	1632	1593	1714	1783	1843	1685
Calcium cyanamide	2907	1638	1401	1170	1534	1254	2011	1968	1634
Nicifos	1985	1337	1390	1818	1320	1339	2044	1807	1630
Complete fertiliser	2019	1680	1915	1407	1345	1399	1784	1810	1670
No fertiliser	1882	1881	1103	1744	1559	1694	2105	1856	1728
Mean of each block	1940	1639	1478	1516	1505	1536	1920	1869	1675

Other phases studied are tillering and filling of earheads as indicated by data in Tables XVI and XVII.

TABLE XVI

Number of earheads (different classes) per plot

Number of Block	Class of the Earheads	Sulphate of ammonia	Nitrate of soda	Calcium cyanamide	Nicifos	Complete fertiliser	No fertiliser	Mean of each block
1B	Fully filled	1716	1453	2585	2011	2440	2660	2144
	Half filled	488	1051	218	575	630	450	569
	Blank	949	312	442	850	450	360	561
2B	Fully filled	2055	1911	1918	1231	1657	1805	1763
	Half filled	405	387	242	403	395	496	388
	Blank	330	695	575	153	830	640	537
3B	Fully filled	1142	2053	1544	1625	1780	1764	1651
	Half filled	836	427	378	134	941	98	469
	Blank	288	440	353	299	352	403	356
4B	Fully filled	1735	1750	1656	1586	1866	2293	1814
	Half filled	440	715	168	420	325	800	478
	Blank	380	325	423	915	416	395	476
5B	Fully filled	1770	1286	1903	1416	1410	1200	1498
	Half filled	310	635	589	176	530	744	497
	Blank	410	1302	661	625	627	1003	771
6B	Fully filled	1806	1860	1407	1426	1640	1888	1671
	Half filled	450	745	543	789	752	633	652
	Blank	489	427	506	197	295	330	374
7B	Fully filled	2297	2559	2042	2285	2292	2150	2278
	Half filled	138	660	284	630	177	385	379
	Blank	562	444	511	208	511	395	439
8B	Fully filled	1552	1518	2011	2023	1666	1625	1733
	Half filled	354	715	409	516	166	1225	564
	Blank	260	675	267	126	598	325	375
Mean of Eight Blocks	Fully filled	1759	1799	1883	1700	1831	1923	
	Half filled	423	669	354	455	490	604	
	Blank	459	598	467	422	510	481	
Percentage of total number of earheads	Fully filled	66	58	69	65	64	63	
	Half filled	16	22	13	18	17	20	
	Blank	17	19	17	16	18	16	

TABLE XVII

Number of earheads per plant or tillering

Treatment	Block 1B	Block 2B	Block 3B	Block 4B	Block 5B	Block 6B	Block 7B	Block 8B	Mean of 8 Blocks
Sulphate of ammonia	1.58	1.84	1.46	1.96	1.49	1.48	1.68	1.13	1.58
Nitrate of soda	1.70	1.71	1.97	1.73	2.04	1.80	2.06	1.59	1.83
Calcium cyanamide	1.55	1.68	1.65	1.94	2.08	1.97	1.42	1.43	1.73
Nicifos	1.74	1.36	1.49	1.63	1.70	1.84	1.53	1.48	1.59
Complete fertiliser	1.75	1.73	1.62	1.88	1.92	1.94	1.69	1.35	1.74
No fertiliser	1.85	1.57	2.08	2.02	1.91	1.77	1.39	1.72	1.79
Mean of each block	1.70	1.65	1.71	1.86	1.86	1.80	1.63	1.45	1.71

Nitrate of soda has generally given slightly higher tillering while sulphate of ammonia and nicifos have generally been low in this respect.

Some tendency of a large number of plants being associated with less tillering is noticeable when individual plots are examined.

Nitrate of soda has given the least and calcium cyanamide the largest proportion of fully filled earheads.

One important factor which contributes to the yield of grain is also the weight per earhead. A study of this from observations as recorded in Table XVIII reveals :

TABLE XVIII

Average weight per fully filled earhead in tolas

Treatment	Block 1B	Block 2B	Block 3B	Block 4B	Block 5B	Block 6B	Block 7B	Block 8B	Mean of 8 Blocks
Sulphate of ammonia	0.48	0.62	0.82	0.71	0.50	0.80	0.65	0.75	0.67
Nitrate of soda ..	0 61	0.72	0.72	0.72	0.64	0.57	0.57	0.69	0.66
Calcium cyanamide ..	0.43	0.55	0.79	0.70	0.53	0.66	0.73	0.56	0.62
Nicifos..	0.52	0.69	0.69	0.61	0.57	0.76	0.69	0.54	0.63
Complete fertiliser ..	0.52	0.68	0.51	0.66	0.57	0.67	0.65	0.70	0.62
No fertiliser ..	0.45	0.59	0.62	0.52	0.54	0.68	0.64	0.59	0.58
Mean of each block	0.50	0.64	0.69	0.65	0.56	0.69	0.66	0.64	0. 68

(1) The weight per earhead is more or less in the inverse proportion to the number of earheads or in other words the number of bearing plants.

(2) The fertilisers have been able to increase the weight per earhead over the one in compensation for the number of earheads per unit area, sulphate of ammonia and nitrate of soda being higher than others in this respect.

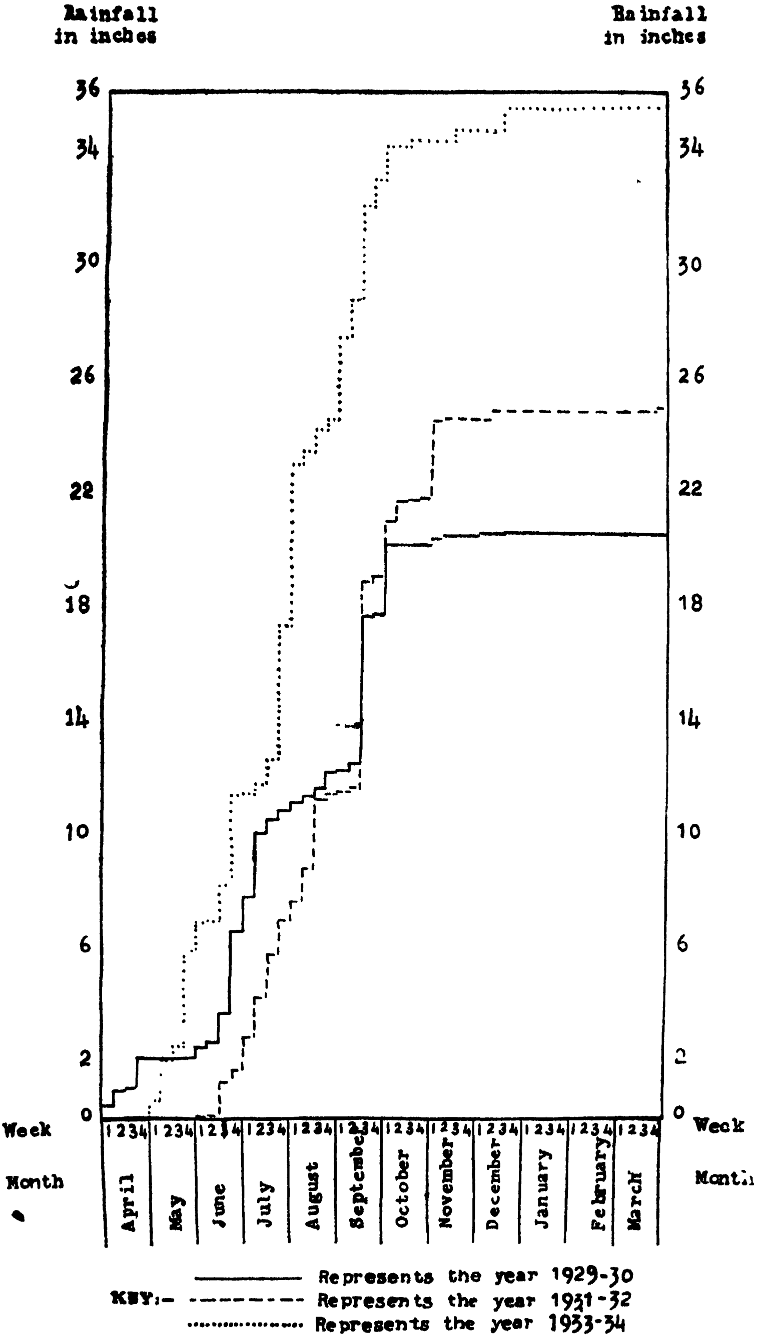


Fig. 1. Rainfall by weekly periods for three years during the six years commencing from April 1928 to March 1934.

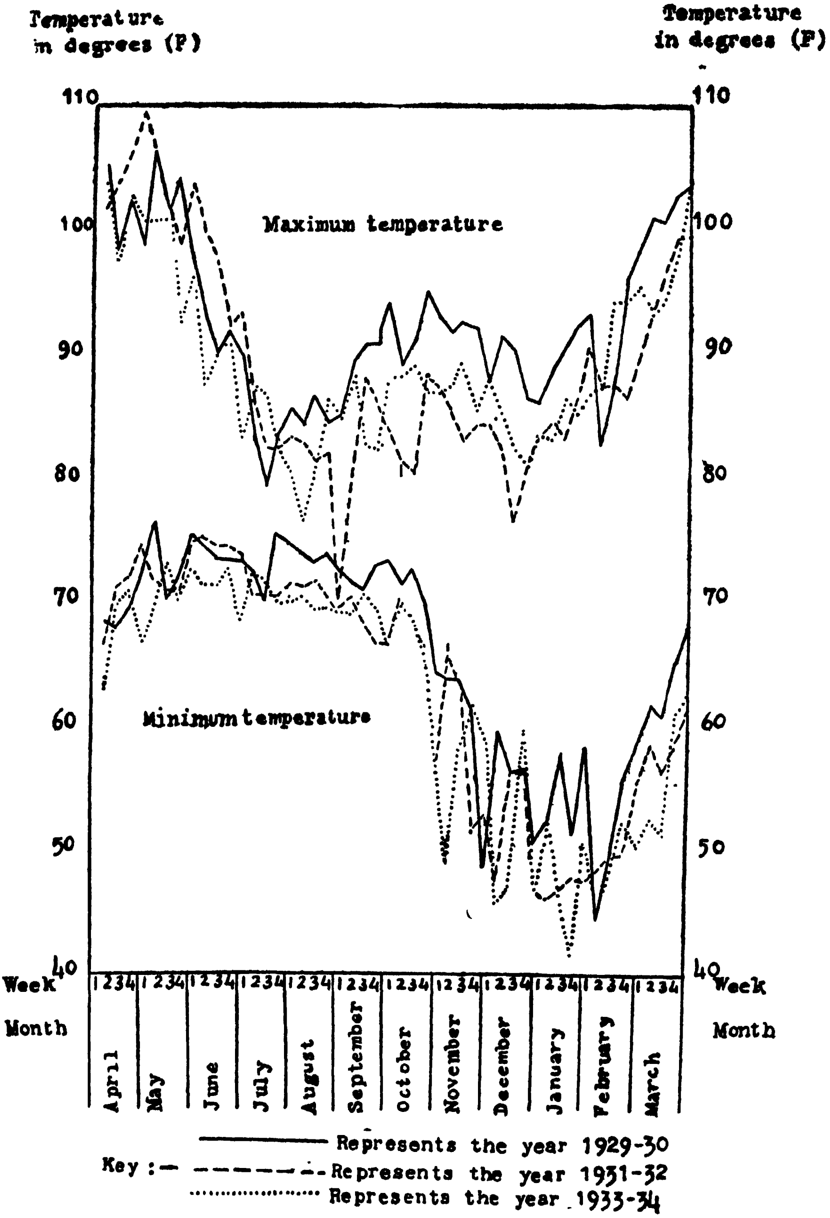
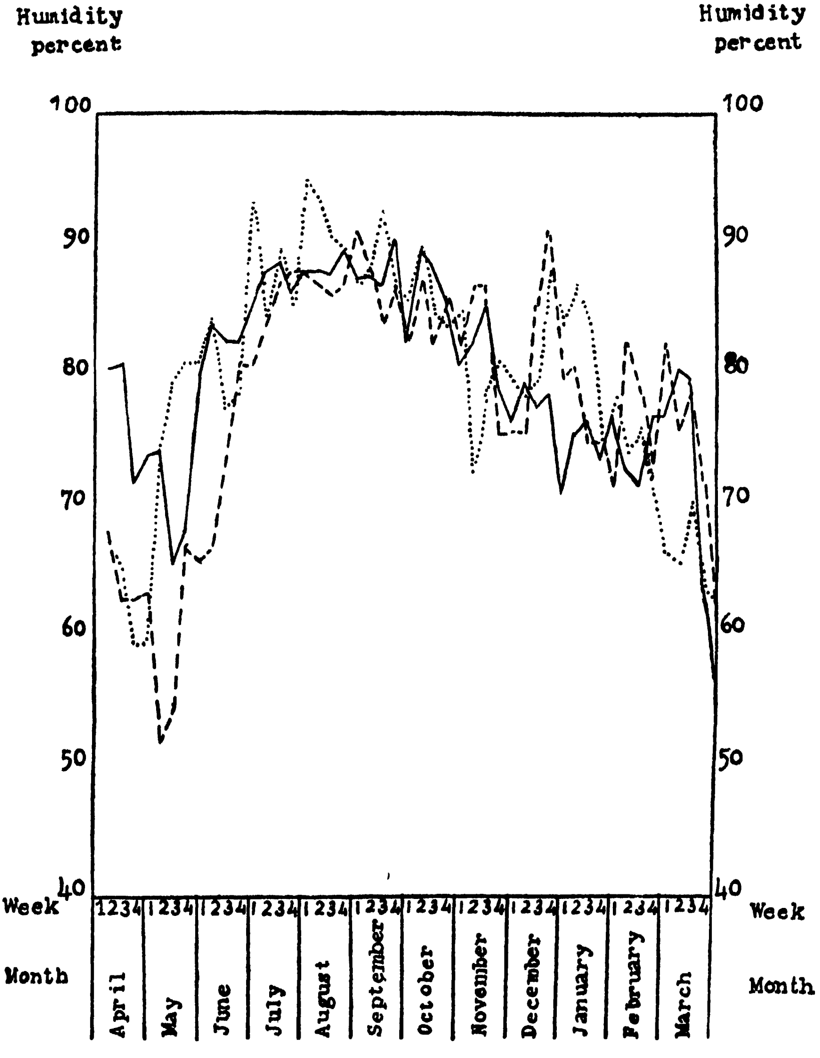
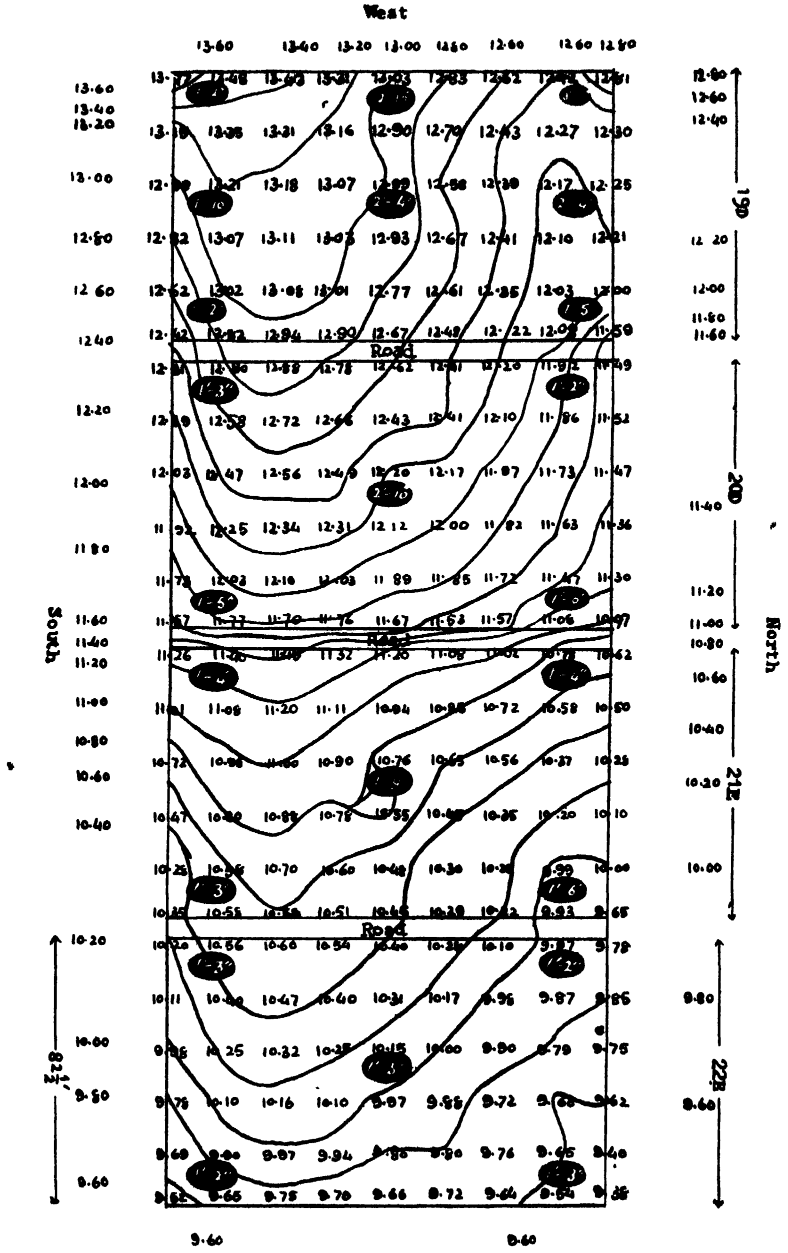


Fig. 2. Maximum and minimum temperature (F) by weekly periods for three years during the six years commencing from April 1928 to March 1934.



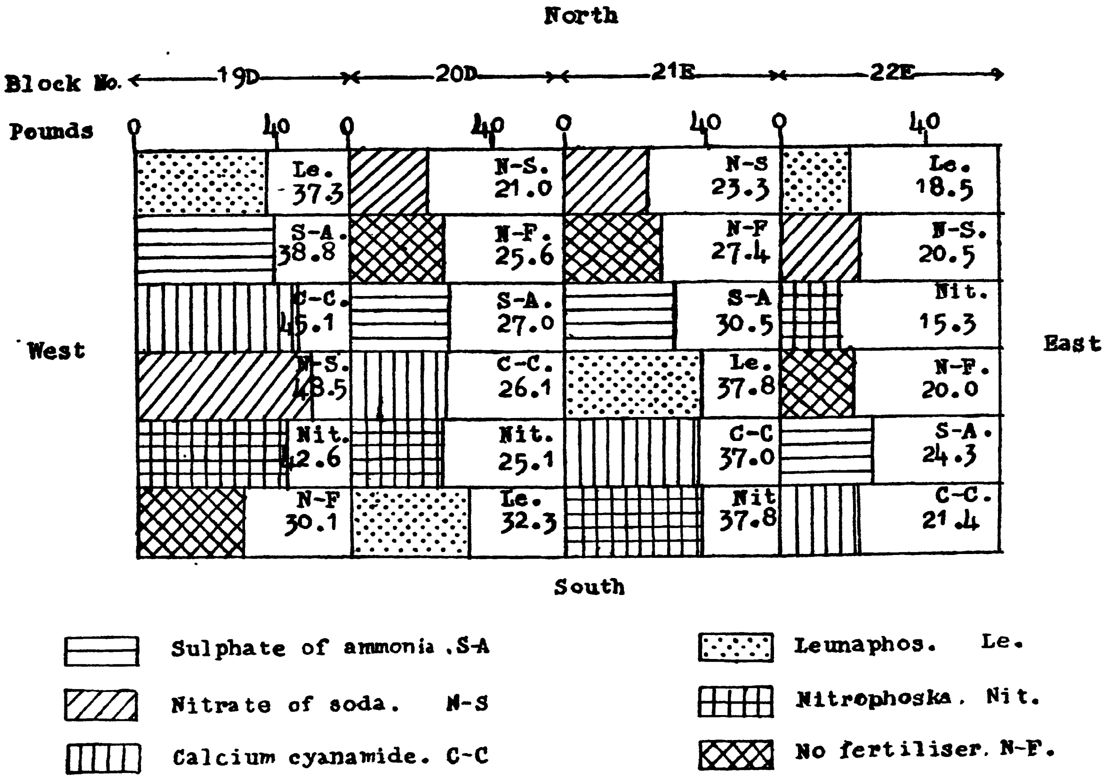
KEY:— ———— Represents the year 1929-30
– – – – – – Represents the year 1931-32
………… Represents the year 1933-34

Fig. 3. Humidity by weekly periods for three years during the six years commencing from April 1928 to March 1934.



Bajri crop—1929-30

Fig. 4. Contours of levels and depths of soil (as indicated by the encircled figures in feet and inches) up to the murum layer in blocks 19D, 20D, 21E and 22E.



Bajri 1929—30

Fig. 5. Situation of different treatments and yield per plot in pounds.

THE ALGAL FLORA OF TEMPORARY WATERS AROUND BOMBAY

I. An Ecological Study of the Algae in some Rain-water Pools at Borivli

By

ELLA A. GONZALVES, B.A., M.Sc.,

AND

DWARKA B. JOSHI, M.Sc.

Botany Department, Royal Institute of Science, Bombay

INTRODUCTION

TEMPORARY waters such as rain-water pools, road-side ditches, etc. as a rule harbour a considerable bulk of algal growth. The importance of a study of such algae was realised over 35 years ago by Fritsch (1907) who surveyed the algae of rock pools and of road-side ditches and lowland pools in Ceylon, and found a difference in their respective algal compositions. In India, Iyengar (1938) has also emphasised the interesting nature of such waters. He observed that there are two types of temporary waters, *viz.*, 1) rain-water pools which are filled immediately after the first showers of rain and which dry up soon after the rains or after a prolonged spell of dry weather, and 2) small pools or ponds which are dry towards the close of the hot season. Iyengar (1940) has also studied the algal flora of muddy rain-water pools in Madras. In Northern India, Singh (1940) has recorded some observations on the biological productivity of rain-water pools.

The algae which live in such situations are subject to conditions quite different to those which the algae of permanent waters or larger pieces of temporary waters have to endure. In the first place the danger of desiccation is very great, as the pools dry up very quickly. Hence changes in the concentration of the water are rapid. Secondly, in order to tide over a dry spell, or to survive from one year to the next, they must have the power of doing so either in the dried vegetative condition, or they must be able to complete their life-cycle and form resting spores in the short time when conditions are favourable to their growth. Thus the germination of the spores, growth and development, and reproduction must be condensed into a very short period. As the algae can only flourish in a particular situation when there is a perfect state of harmony between themselves and their environment, it would be interesting to note the ecological factors operating in these small pieces of water and influencing algal growth. A study of such pools would also show what groups or types can thrive best in them.

In this investigation the algae in a group of pools were studied during the monsoons of two successive years, in order 1) to see if such pools harbour the same type of algae throughout the season or whether there is any succession in them, 2) to see if there is any correlation between the occurrence of the algae and the climatic conditions such as rainfall, temperature and hours of bright sunshine, and 3) to study the methods adopted by these algae to secure their perennation.

GENERAL DESCRIPTION OF THE POOLS

The pools were situated at Borivli which is 22½ miles north of Bombay on the B.B. & C.I. Railway. About a mile from the station was a mass of rock on the top of which were 6 to 8 small natural depressions. These cavities were scarcely a foot in diameter and 6 to 12 inches in depth. They were not deep like the rock pools of Fritsch (1907) and none of them owed their origin to springs ; but they were filled with water during the monsoon when they were found to contain a rich growth of algae. The substratum being rock, there was scarcely any natural soil at the bottom, but the abundant algal growth which dried at the end of the season collected in the hollows.

METHOD

Systematic collections of the algae were made once a fortnight during the rainy seasons of 1939 and 1940 till the pools dried up. The algae were identified and the frequencies of the various species noted. The symbols used by Fritsch and Rich (1913) were also used here. The numerical values were the same as those adopted by Howland (1931), viz. those obtained from counts of individuals found in 50 fields of the microscope under a magnification of 350. The following symbols * were employed :—

i=1, vr=1—5, r=5—10, rc=10—20, c=20—30, vc=50—100,
a=100—200 and va=200—400.

The frequencies of the filamentous algae could not be determined accurately, but they were estimated roughly from the amount present in each collection. The meteorological data were obtained from the Colaba Observatory, Bombay, and are given in Table I. The fortnightly average temperature was calculated from the maximum and minimum temperatures each day. The fluctuations in average temperature were slight and throughout the season varied within a few degrees. The fortnightly average sunshine value was calculated from the values of daily hours of bright sunshine. The rainfall for the fortnight represents the

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* The meaning of the symbols is as follows :—
i=isolated, vr=very rare, r=rare, rc=rather common,
c=common, vc=very common, a=abundant, va=very abundant.

total rainfall received during the fortnight. In Bombay from July to September there is fairly heavy rain, and therefore during these months there is always water in the pools. The concentration of the water varied according to the amount of rainfall and days of bright sunshine. The investigation commenced in June 1939, the first collection being made towards the end of June. The following year, collections were made again to see if there was any change in the algal composition and in the time of appearance of the various forms.

TABLE I

Months	Hours of Sunshine		Rainfall		Temperature	
	1939	1940	1939	1940	1939	1940
June 1—15 ..	7.38	7.56	3.06	4.72	84.98	85.34
„ 16—30 ..	5.79	3.33	1.61	25.28	84.575	81.59
July 1—15 ..	0.48	0.85	31.02	3.71	80.64	82.9
„ 16—31 ..	2.08	2.686	2.06	17.93	81.85	81.33
Aug. 1—15 ..	6.14	2.68	1.26	14.77	82.51	81.04
„ 16—31 ..	0.587	4.2	10.55	12.57	79.175	79.82
Sept. 1—15 ..	4.44	8.73	1.47	1.00	80.5	83.35
„ 16—30 ..	6.85	6.68	3.14	10.26	81.38	80.61
Oct. 1—15 ..	8.16	7.32	0.00	2.18	81.36	83.46
„ 16—31 ..	9.95	9.08	0.16	2.21	83.58	82.6

THE ALGAE OF THE POOLS

The following is the list of algal species observed in the pools during the monsoon of June 1939 :—

I. CHLOROPHYCEAE (ISOKONTAE)*

Chlorococcales:—1) *Pediastrum duplex* Meyen, 2) *Scenedesmus brasiliensis* Bohlin, 3) *S. obliquus* (Turpin) Kütz., 4) *Ankistrodesmus falcatus* (Corda) Ralfs, 5) *Coelastrum cambricum* Archer.

Ulotrichales :—6) *Schizomeris Leibleinii* Kutz.

Oedogoniales :—7) *Oedogonium quadratum* Hallas, 8) *Oe. dioicum* Carter, 9) *Oe. Intermedium* Wittr., 10) *Oe. bengalense* Hirn, 11) *Oe. oelandicum* Wittr. Hirn forma *minus* Borge.

Conjugales :—12) *Spirogyra plena* (W. & G. S. West) Czurda, 13) *Sirogonium ceylanicum* Wittr., 14) *Mougeotia laetivirens* (A. Br.) Wittr., 15) *Closterium eboracense* Turner, 16) *C. acerosum* (Schrant) Ehr., 17) *Cosmarium polygonum* (Nag) Arch., 18) *C. Lundelii* Delp.

II. EUGLENINEAE

19) *Euglena proxima* Ehr.

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* The classification adopted is that of Fritsch in "The Structure and Reproduction of the Algae"—1935.

III. MYXOPHYCEAE (CYANOPHYCEAE)

20) *Coelosphaerium Kuetzingianum* Näg., 21) *Microcystis aeruginosa* Kütz., 22) *Aphanothece Castagnei* (Bréb) Rab., 23) *Lyngbya majuscula* (Dillw.) Harvey, 24) *Nostoc sp.*, 25) *Anabaena Fuellebornii* Schmidle., 26) *A. oscillarioides* Bory., 27) *Dichothrix gypsophila* Kütz., 28) *Gloeotrichia Raciborskii* Wolos.

The next year almost the same forms occurred again, though not at the same time. The exceptions were *Ankistrodesmus falcatus*, *Gloeotrichia Raciborskii* and *Coelosphaerium Kuetzingianum* which did not appear. Instead a few other forms such as *Zygnema cyanosporum* Cleve, *Oscillatoria subbrevis* Sch., *Calothrix scytonemicola* Tilden and a few members of the Chlorococcales such as *Sorastrum Americanum* (Bohlin) Sch., *Tetraedron regulare* Kütz. and *T. muticum* (A. Br.) Hansg. made their appearance. The last occurred as a sudden bloom at the end of the season. Thus in 1940 the total number of species was 31. The number of floating filamentous forms was greater than that of the unicellular forms, but there were hardly any attached ones. The majority of the species belonged to the Chlorococcales, but except on a few occasions, they were never common. *Oedogonium* and *Spirogyra* were abundant in all the pools. Some other members of the Zygnemaceae were also dominant in the pools for some time. Tables II and III show the numbers of algae belonging to the different classes in the two seasons.

TABLE II

Date	Chlorophyceae	Cyanophyceae	Euglenineae	Total
13-6-39	7	2	1	10
7-7-39	6	2	1	9
21-7-39	11	4	1	16
4-8-39	13	4	1	18
18-8-39	19	2	..	21
1-9-39	15	4	..	19
14-9-39	11	8	..	19
1-10-39	9	9	..	18
10-10-39	5	9	..	14

TABLE III

Date	Chlorophyceae	Cyanophyceae	Euglenineae	Total
25-6-40	4	..	1	5
9-7-40	14	..	1	15
23-7-40	18	1	1	20
10-8-40	20	2	1	23
20-8-40	20	1	..	21
3-9-40	15	2	..	17
17-9-40	13	5	.	18
1-10-40	4	8	—	12
15-10-40	5	8	—	13

Though the total number of forms was approximately the same in the two years, it is clear from the Tables that more forms occurred at one time in 1940 than in 1939. Again the maximum number of green algae was reached much later in 1939. In 1939, 21 forms were obtained about the middle of August, while in 1940, 20 forms were seen in July, almost a month earlier, and the maximum, *viz.*, 23 forms, almost in the first week of August (*cf.* Fig. 1, and Tables II & III).

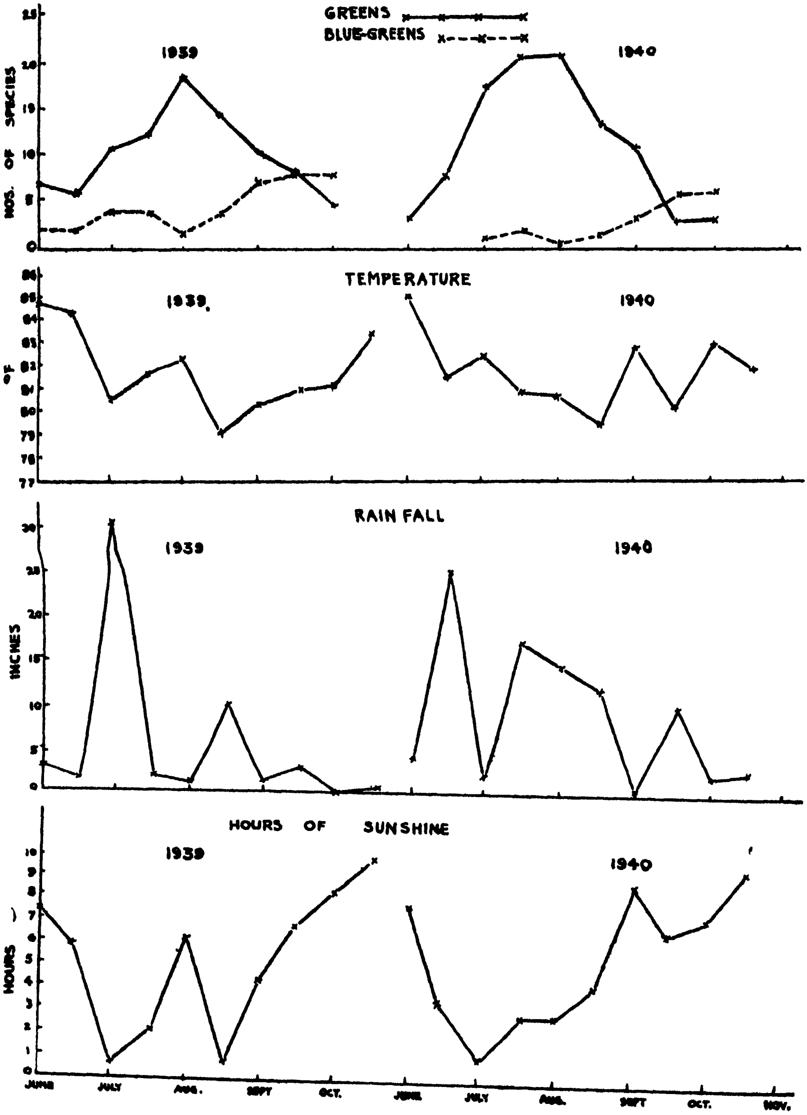

FIG. 1. Graphs showing the relative numbers of algae and the meteorological data for the rainy seasons of 1939 and 1940.

SUCCESSION OF THE ALGAE

The algae could be divided into three groups, *viz.*, those which flourished at the beginning, those which occurred towards the middle and those which were seen at the end of the monsoon. The frequencies of some of the algae in the pools are given in Table IV.

TABLE IV

	939									1940								
	June 23rd	July 7th	July 21st	Aug. 4th	Aug. 18th	Sept. 1st	Sept. 14th	Oct. 1st	Oct. 10th	June 25th	July 9th	July 23rd	Aug. 10th	Aug. 20th	Sept. 3rd	Sept. 17th	Oct. 1st	Oct. 15th
1) *Schizomeris Leibleinii* ..				vr	r	c	i				rc	rc	c	vc	c	vr		
2) *Oedogonium dioicum* ..	c	! rc	rc	rc	r	r	vr			a	!va	c	c	c	r	r	i	
3) *Oedogonium oelandicum forma minus*					c	c	! vc	a	c				r	rc	c	!va	vc	i
4) *Spirogyra plena* ..			r	rc	!vc	c	c	rc	r		rc	vc	! a	vc	vc	rc	c	vr
5) *Zygnema cyanosporum* ..											c	!a	a	rc	rc			
6) *Sirogonium ceylanicum* ..	i	i			vr	! c	c	c				c	rc	!c	vc	a	a	c
7) *Mougeotia laetivirens* ..				r	!rc	r	r						i	r	!a	rc	r	
8) *Closterium eboracense* ..			i	a	rc	r	r	r		i	r	rc	a	i				
9) *Cosmarium polygonum* .	vr	vr	vr	r	a	rc	c	r		i	i	i	rc	a	c	i		
10) *Aphanothece Castagnei* .	r	rc	i	i	i	r	vc	vc	c							c	c	r
11) *Nostoc sp.* .			c	rc		rc	vc	c	c						c	c	c	c
12) *Anabaena Fuelleborii* ..						r	r	c	c						r	r	c	vc

! represents sexual reproduction.

To the first group belonged all the species of Oedogonium (except *Oe. oelandicum*), *Zygnema cyanosporum*, *Scenedesmus obliquus* and *Euglena proxima*, all of which were seen very soon after the rains. They rapidly reached their maximum during July and either disappeared by the beginning of September or persisted till the end of the season as isolated forms. *Oedogonium* was dominant at this period and formed oogonia and oospores quite early, by the end of June or the beginning of July. Almost all the species were more abundant in 1940 than in 1939. *Zygnema cyanosporum* which appeared only in 1940 also reached its maximum in July when zygospores were formed. *Scenedesmus obliquus* disappeared entirely by the middle or the end of July. Of the blue-greens, only *Aphanothece* was seen in appreciable numbers at the beginning of the season in 1939. *Euglena* was common in the early days of the monsoon, and then its numbers declined. The conditions thus favourable for these forms were abundant rain and not much sunshine.

The majority of the green algae however belonged to the second group. They made their appearance when a spell of bright weather ensued after the first heavy showers of rain. *Spirogyra plena* appeared in July, reached the high water mark of its development in the middle of August, and maintained a vigorous growth till September. It was only in October that its numbers diminished. *Mougeotia laetivirens* had a shorter span of life. It appeared in the middle of August and was rare by the middle of September. Rare filaments of *Schizomeris* were likewise seen in the middle of July in 1939, but this type disappeared in September. In 1940 it appeared much earlier as a rather common form in the beginning of July, became very common by the middle of August and disappeared by the middle of September. All the desmids reached their maximum in the third week of August, and then declined. *Cosmarium polygonum* was seen throughout the season. The other green algae, though never seen in large numbers in either year, also belonged to the second group. The conditions favourable for the second group of forms seemed to be less rain and more sunshine.

The third class includes almost all the blue-greens. With the exception of Nostoc which appeared earlier, all the other blue-greens developed in the middle of September or a little earlier and were dominant by the end of the season. *Aphanothece* was present at the beginning of the year in 1939, but appeared very late in 1940. Its late appearance in 1940 can be attributed to the following reasons. In 1939 there was very little rain when the monsoon broke, and so the pools were filled with just sufficient water for this form to develop. As soon as there was heavy rain, as during the first fortnight of July, the water became very dilute and hence the form became "isolated." When the water became more concentrated at the end of the season, it appeared again. In 1940 the rainfall was very heavy almost from the commencement of the monsoon, and the form did not get a chance to develop, as the water in the pools was very dilute. Hence it only occurred at the end of the season. Tetraedron muticum appeared suddenly in very large numbers at the end of September. The reason for this sudden bloom was not apparent. *Oedogonium oelandicum* and *Sirogonium ceylanicum* were two forms which occurred somewhere in the middle of the season, but were common even at the end of the rains and so could be placed in the third class. The conditions of development for the third group were concentrated water, long hours of sunshine and high temperature.

Though the life-histories of all these forms were restricted to a few months, yet during this period the conditions that favoured the appearances of the green algae were not the same as those which suited the blue-greens. The former were seen at the beginning of the season in small numbers. They flourished till the middle of the monsoon and then declined, whereas the latter appeared in the middle or towards the close of the season and rapidly rose in number, maintaining their greatest number at the end of the season.

A comparison of the weather conditions in the two years brings out the following points. In 1939, the total rainfall was 54.33 inches while in 1940 the total was 94.63 inches. Moreover the fortnightly maximum rainfall was recorded in the middle of July in 1939, but in the beginning of July in 1940. The hours of bright sunshine were inversely proportional to the amount of rainfall. This was observed throughout the season in both years except in the middle of July in 1940 when the figures for both rainfall and the amount of bright sunshine were low. The sky however at this time was very cloudy and that is why, though no rain actually fell, the number of hours of sunshine was reduced. If a comparison is made between the graph showing the number of green algae and that of rainfall and sunshine (*cf.* Fig. 1), it is obvious that the greatest number of algae appears when there is a period of dry weather after a spell of heavy rain. The reason for the early development of certain forms in 1940 thus becomes clearly apparent. The fortnightly maximum rainfall as mentioned above was recorded in the latter half of July in 1939, and in the early half of the same month in 1940. Thus in 1939, the green algae reached their maximum number about a month after the maximum rainfall, *i.e.*, in the middle of August when there was also a rise in the hours of sunshine, after which they steadily declined. The second rise in the hours of bright sunshine had no effect on the green algae as the condition of the water was now inhibitory to their growth. Low concentration of the water combined with moderate hours of sunshine thus favoured the development of the green algae. In 1940 the maximum number was obtained also about a month after the maximum rainfall, and hence much earlier than in the previous year.

When the hours of bright sunshine increased and the temperature was high, the water became more concentrated and the conditions were ideal for the blue-greens which appeared at the end of the season. This fact has been observed by practically all workers in algal ecology. Though a number of green forms were seen at the end of the season most of them were isolated and only one or two were in appreciable numbers.

COMPARISON WITH OTHER POOLS

In Ceylon Fritsch (1907) found that in road-side ditches and lowland pools, the Conjugales were the dominant group and *Spirogyra* was the most usual form. A subsidiary vegetation usually composed of *Oedogonium* was often present. In a few cases *Oedogonium* was dominant and *Spirogyra* was subsidiary. If both these types were absent, then the Cyanophyceae took the lead, though as a rule, they were not well represented. Desmids (filamentous in particular) were occasionally very abundant, but other colonial and unicellular forms like the Chlorococcales were rare. The *Oedogonium-Spirogyra* association was the most constant feature of the road-side pools of Ceylon. In the rock-pools (pools found in huge masses of basalt) the Cyanophyceae were decidedly in the majority—particularly in the shallower pools. When not dominated by the Cyanophyceae, there was a rich growth of green algæ consisting mostly of members of the Conjugales and Chlorococcales. *Oedogonium* played a minor part and only attained considerable development in one or two pools. Of the Conjugales, certain species of the Zygnemaceae and Desmidiaceae were abundant and *Spirogyra* was a subsidiary form, and *Zygnema* more important. Filamentous desmids were common. The desmids of the rock-pools were more complex in form than those of the road-side.

The *Oedogonium-Spirogyra* association in these pools shows that the flora of these pools approaches more closely that of the road-side and lowland pools of Ceylon than that of the rock-pools. The only resemblance to the latter is in the presence of the Cyanophyceae, which however only occur here at the end of the season. These pools are thus more of the nature of road-side puddles, and the rocky substratum has no remarkable effect on the flora. A noteworthy feature is the absence of the Volvocales which Iyengar (1938, 1940) found to be predominant in small pools in Madras ; but as Fritsch (1907) has not observed them to play an important part in the road-side pools of Ceylon, their absence is not surprising. Iyengar (1938) also noticed that the same algae cropped up in these pools if there are successive spells of dry and wet weather, but towards the end of the season, the Euglenineae and the Cyanophyceae replaced the Chlorophyceae. The blue-greens, however, play a subordinate rôle in such waters. Singh (1940) found that the Cyanophyceae constituted the greater part of the flora of rain-water pools in Northern India. In these pools both the greens and the blue-greens are equally important, the former at the beginning of the season, the latter at the end. Except for *Euglena proxima* at the beginning of the season, the Euglenineae are also poorly represented.

METHODS OF PERENNATION

With regard to the Oedogoniales, all the species formed oogonia at the earliest possible stage—in fact, the young vegetative filaments were seen to form oogonia almost at the beginning of the season. The early formation of oogonia belies the usual view that vegetative growth occurs when conditions are favourable, and reproduction takes place when adverse conditions are setting in. *Oedogonium oelandicum*, however, formed oogonia in the middle or the latter half of September probably due to its late appearance. There were two maxima in the rainfall graph, and this form produced oogonia after the second rise, while the others did so after the first. It probably needed more concentrated water for sexual reproduction, which took place at the end of vegetative activity.

All the Zygnemaceae formed zygospores in the middle of August and with slight differences almost at the same time in both years. The conditions for zygospore formation seemed to be the same as those for maximum vegetative growth. *Schizomeris Leibleinii* was seen to form aplanospores in August at the same time as the Zygnemaceae. Of the desmids, only *Closterium acerosum* conjugated in the middle of the season, about the first week of September. The other three persisted till the end of the season in the vegetative state. West (1909) has remarked that different desmids require diverse conditions for zygospore formation and probably that is why only one species conjugated here. Hodgetts (1921) observed that while moderate amounts of bright sunshine are sufficient for good vegetative development of desmids, abundant bright sunshine is necessary for conjugation, particularly of *Closterium acerosum.* He found *Closterium acerosum* in conjugation when the daily mean, in hours of bright sunshine, was about 7 hours per day. In this case *Closterium acerosum* conjugated when there was about the same amount of sunshine per day, *viz.*, 8 hours which is moderate for India. The other desmids probably needed stronger sunshine for conjugation. The hours of sunshine in September were high enough for vegetative development of the other desmids but not sufficiently high for conjugation. Moreover the majority of the desmids was crowded out by the filamentous forms before the conditions requisite for conjugation were realised in the pools. In October when the meteorological conditions were ideal for conjugation, the pools dried up very quickly and time acted as a limiting factor, preventing conjugation.

When the pools were dry, a little of the mud from the bottom was taken and examined. The dried vegetative cells of the desmids were seen in the mud. Some of the mud was placed in water in jars in the laboratory, but though the desmids showed signs of revival, they were not able to flourish for a long time. Iyengar (1938) has also seen that some desmids cope with unfavourable conditions in their dried vegetative state. Probably in these pools also, they may be surviving in the same way.

It has been observed that as a rule, only a few species of desmids conjugate to survive winter. In Bombay after the rains, heat and not cold is encountered and the former is more harmful than the latter. It is therefore possible that a good number of the desmids perish at the close of the season in these small collections of water, and that a re-immigration takes place the next year from the bigger pieces of water nearby. As the majority of the Chlorococcales was seen as stray specimens in the pools, it is possible that they too may be coming into the pools from the neighbouring ponds.

Of the blue-greens, the following formed resting spores at the end of the season, *viz.*, *Gloeotrichia Raciborskii*, *Anabaena Fuellebornii*, *A. oscillarioides* and *Dichothrix gypsophila.* The other spore-bearing forms were unable to form spores and probably resisted the dry season in the form of hormogonia. Biswas (1925) records that the blue-green algae which grow on road-side paths etc. can resist prolonged desiccation. Their mucous sheaths gradually lose water and shrivel up and the dried encrustations become reduced to powder and are blown about by wind. When water is available, the dried cells regain their vegetative activity. The hormogones of forms like *Lyngbya* are protected by the persistent sheaths of the parent filaments, while the protoplast itself exhibits a wonderful capacity to withstand desiccation. In these pools, the filaments of *Nostoc*, *Lyngbya* and the colonial Cyanophyceae were found to dry up at the end of the season and it is probable that they adopt the above means of tiding over the dry period.

SUMMARY

1) The succession of the algae in a group of rainwater pools around Bombay during two monsoons was noted and the occurrence of the algae correlated with the meteorological conditions.

2) The Chlorophyceae were found to predominate at the beginning and the middle of the season, the conditions for their good development being low concentration of water, moderately high temperature and moderate hours of bright sunshine.

3) Towards the close of the season the Cyanophyceae were abundant, replacing the Chlorophyceae, the conditions for their good growth being high concentration of water, high temperature and more hours of sunshine.

4) The differences between these pools and the pools in other parts of India and of Ceylon are noted.

5) The methods of perennation of the various species are discussed.

DESCRIPTION OF THE PLATE

Plate I. A few of the more common algae found in the Borivli pools.
Fig. 1a. *Schizomeris Leibleinii* Kutz × 406.
,, 1b. ,, ,, ,, (aplanospore formation) ×406.
,, 2. *Oedogonium quadratum* Hallas , (formation of oospores) ×182.
,, 3. ,, *intermedium* Wittr.(,, ,, ,,)×182.
,, 4. ,, *oelandicum* Wittr, Hirn. forma *minus* Borge × 406.
,, 5. ,, *bengalense* Hirn. ×782.
,, 6a. ,, *dioicum* Carter female filament × 182.
,, 6b. ,, ,, ,, male filament ×1 2.
,, 7. *Zygnema cyanosporum* Cleve ×55.
,, 8. *Spirogyra plena* (W. & G. S. West) Czurda. ×35.
,, 9. *Mougeotia laetivirens* Wittr. ×182.
,, 10. *Sirogonium ceylanicum* Wittr. ×35.
,, 11. *Tetraëdron muticum* (A. Br.) Hansg. forma *minor* Reinsch. ×406.

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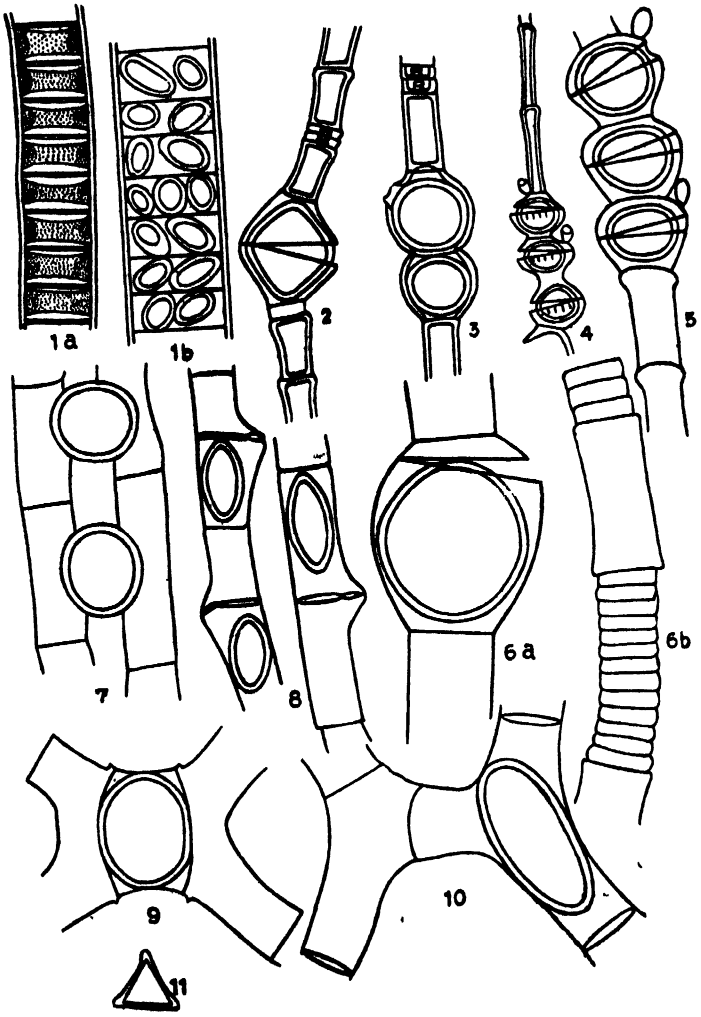


PLATE I

The Algal Flora of Temporary Waters around Bombay.
A few of the more common algae found in the Borivli pools.

A COMPARATIVE ACCOUNT OF CARBON DIOXIDE EXCRETION THROUGH THE SKIN IN SOME VERTEBRATES

By

J. C. George,

Department of Biology, Wilson College, Bombay

INTRODUCTION

IT is a well-known fact that carbon dioxide is excreted through the skin in animals. While this mode of elimination of the gas is clearly manifested in animals without special respiratory organs, it has receded to the background in others.

It is known that protozoons, sponges, cœlenterates and a large number of worms which live in a liquid or moist environment give out carbon dioxide by diffusion to the surrounding medium from their body surfaces. The moist skin consisting of an epidermis and a cuticle in the earthworms, which is richly supplied with blood from inside, is one of the best examples wherein the skin is the chief organ for carbon dioxide excretion. Such an elimination is also met with in the molluscs and echinoderms though some of them possess outgrowths from the integument, which are mainly responsible for that function. In the arthropods the thick cuticle does not permit such free diffusion and the major portion of the carbon dioxide produced in the body is given out through tracheæ in tracheate arachnids and insects, gills in crustaceans and book gills or lung books in other arachnids. Even so it has been shown that in the stick insect Dixippus 25% of the total output escapes through the skin.

The moist skin of the frog shows a high degree of permeability to gases and as such plays an important part in respiration. We have a correct estimate of this from the works of Klug (1884) and later of Krogh (1904). The former found that the ratio of carbon dioxide given out by the lungs to that given out by the skin varied in the different specimens investigated by him from 1 : 2.5 to 1 : 4.46. The latter who made a more exhaustive and precise study of respiration in the frog found that in *Rana fusca* at a temperature of 20°C. the average ratio of cutaneous carbon dioxide output to that of the lungs based on experiments conducted throughout the year is 45 : 129. He further observed that more carbon dioxide is eliminated through the skin in *R. esculenta* than in *R. fusca*.

In terrestrial vertebrates cutaneous respiration becomes restricted. But as carbon dioxide diffuses through animal tissues much more rapidly than oxygen, and as the mammals have a large number of glands in the skin an appreciable amount of carbon dioxide is excreted through the skin. C. R. Giuseppi Franchini and Luigi Preti (1908) carried out experiments on their own hands and arms and from the results obtained calculated that the whole body gives out at 36°C. 4.8 litres of carbon dioxide in 24 hours, which amount is about 1% of that given out in pulmonary respiration. While the elimination of carbon dioxide through the skin in mammals has been recognised, it has been regarded as negligible in reptiles and birds which possess a non-glandular skin. The possibility of an appreciable amount of excretion of carbon dioxide through the skin in these animals, especially the reptiles—the group being intermediate in structure between the amphibians and mammals—was not experimentally tested or even suspected. Having been convinced of its theoretical possibility, I thought of testing it in the common lizard *Calotes versicolor*. By way of comparison it was also estimated in the frog (*Rana tigrina*), rabbit, bat (*Lyroderma lyra*), cat and my hands.

Here I may express my gratitude to my professor Dr. C. J. George who suggested the problem and to Dr. S. C. Devadatta who has given much valuable advice. My thanks are also due to Prof. J. A. Nabar for various suggestions.

EXPERIMENTS

Fig. I illustrates the apparatus used to estimate the carbon dioxide output through the skin as well as that from the whole body, when an animal is in a state of rest. The bulb of tube A contains soda lime. The conical flask B is partially filled with clear, filtered lime water. The jar C holds the animal concerned tied up to a tripod stand. In experiments for testing the total output, the animal is confined in the jar while in those for estimating skin output, its head is made to protrude through a small hole in the lid of the jar. Control experiments are conducted without the animal. The jar C is made airtight by applying sticking plaster and melted paraffin wax around the lid and when necessary around the neck of the animal and other crevices. In the conical flask D is placed clear, filtered lime water. The aspirator jar E is filled with water. B, D and E are also completely made airtight by sealing them with melted paraffin wax. Water is made to trickle down from the aspirator jar by adjusting the clamp attached to the outlet tube. As the water from the aspirator jar is run out, air is sucked into the vacuum formed in the jar. As this air passes through the soda lime in A and the lime water in B, all its carbon dioxide is absorbed and air free from that gas reaches the animal in the jar C. The carbon dioxide given out by the animal is absorbed in the conical flask D by the lime water. The calcium carbonate formed in the flask is filtered out, dried and weighed. No precipitate of calcium carbonate occurred in the flask in the control experiments without using the animal. For emptying eight jars of water (40.56 litres) it takes about four hours, and each experiment lasts for such time.

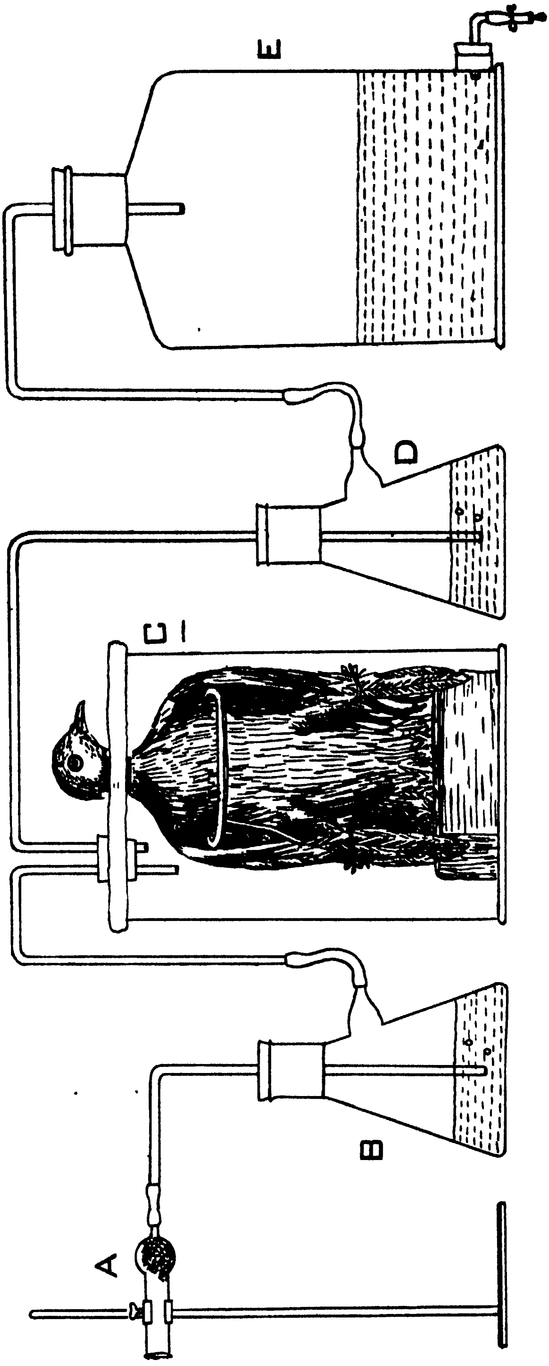
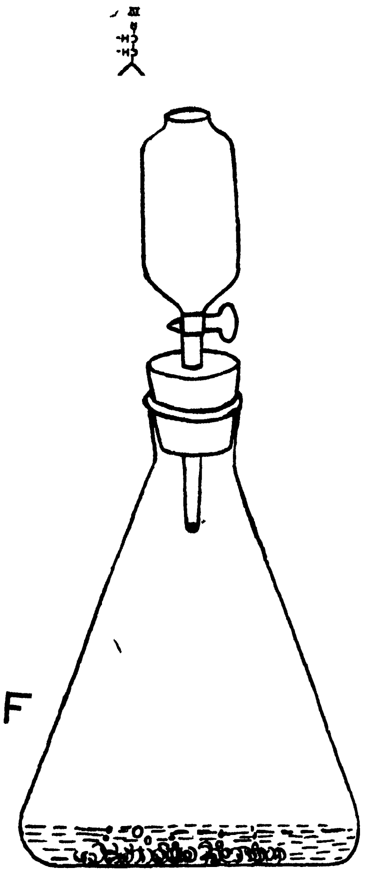


Fig. I



If from the weight of the calcium carbonate precipitated in the lime water the amount of carbon dioxide given out is calculated, there is likely to be some error on account of impurities such as water, keratin released from the animal, and also calcium oxide which may be present in the precipitate. The precipitate is therefore subjected to decomposition by hydrochloric acid and the weight of carbon dioxide released is ascertained. The apparatus used for this purpose is illustrated in Fig. II. The apparatus consists of the conical flask F in the bottom of which is placed the calcium carbonate precipitate. The dropping funnel G is filled with concentrated hydrochloric acid, whose quantity leaves a surplus after decomposing the whole of the precipitate. The apparatus with the acid-filled dropping funnel is first weighed. After this all the acid is dropped from the funnel on the precipitate. The apparatus is kept thus till all chemical action stops. It is then weighed. The loss of weight gives the weight of carbon dioxide evolved from the precipitate.

Fig. II

The following tables give the mean of the results of the various experiments.

Statement giving the cutaneous output of Carbon dioxide per 1000 sq. cms. of body surface in some vertebrates

Animal	Time	Vol. of air passed free from Carbon dioxide in litres	Body Surface area involved in sq. cms.	Wt. of Carbon dioxide in gms. given out through skin	Vol. of Carbon dioxide in c.c. given out through skin at N. T. P.	Vol. of Carbon dioxide in c.c. given out per 1000 sq. cms.
Cat	4 hrs.	40.56	710	0.014	7.1	10.0
Bat	,,	40.56	535	0.019	9.7	18.1
Pigeon	,,	40.56	514	0.030	15.3	29.8
Human Hand ..	,,	40.56	810	0.059	30.0	37.0
Calotes . ..	,,	40.56	128	0.017	8.7	67.9
Frog	,,	40.56	366	0.070	35.6	97.3

Statement giving the pulmonary and cutaneous carbon dioxide output in some vertebrates

Animal	Time	Vol. of air passed, free from Carbon dioxide in litres	Wt. in gms. of Carbon dioxide given out from lungs	Vol. of Carbon dioxide in c.c. given out from lungs at N.T.P. (L)	Vol. of Carbon dioxide in c.c. given out through the skin at N.T.P. (S)	S/L
Frog ..	4 hrs.	40.56	0.031	15.8	35.6	2.253
Calotes ..	,,	40.56	0.020	10.2	8.7	0.853
Bat ..	,,	40.56	0.055	28.0	9.7	0 346
Pigeon ..	,,	40.56	0.393	200.1	15.3	0.076
Rabbit .	..	40.56	0.317	161.4	12.2	0.076

DISCUSSION

The intake of oxygen and the output of carbon dioxide through the skin of animals depend upon the nature of the skin, and the amount of its blood supply. The invertebrate skin is a simple structure consisting of a single layer called the hypodermis. The hypodermis of sponges, cœlenterates and echinoderms consists of a single layer of flat epithelium. In the worms it is ciliated or columnar. The permeable cuticle of the worms is a secretion of the epidermis. Thus constituted, the invertebrate skin is highly permeable to gases, the exception being that of arthropods with thick exoskeleton made of chitin.

Among the chordates the epidermis of the tunicates is much like the hypodermis of the invertebrates in its nature and functions. It also secretes a cuticle which is unique in being supplied with blood vessels. In amphioxus the compound integument of the vertebrates consisting of epidermis and corium is exhibited in its simple form inasmuch as the former consists of only a single layer. The epidermis of the cyclostomes is glandular, thin and without scales. That of fishes is similar, but scaly. The skin of the frog is non-scaly, thin and glandular. Moreover it receives a copious blood supply. That of reptiles and birds is thin, dry and in the former mostly scaly. The mammalian skin is generally glandular, thick and in rare cases with scales. The nature of the skin in the various classes of vertebrates can be summed up in the words of H. E. Walter: "There is a tailored snugness about the skin of the fish that is not apparent in the baggy jacket of the frog, the loose integument of the bird, or the comfortable wrinkles of the mammalian skin."

Compared to the lower invertebrates like the earthworm, the respiratory function of the skin is limited in the vertebrates. This is due primarily to the comparatively thick epidermis which occurs in several layers. Even so, the skin of the frog has been shown to be highly respiratory. There are some salamanders which are lungless and therefore use their skin as the primary respiratory organ. In these amphibians the skin is able to perform its respiratory function so well because it is richly supplied with blood.

From the results of the experiments given above, it is evident that Calotes also utilises its skin as a respiratory organ, since a considerable amount of carbon dioxide is excreted through it. From the dissections carried out we find that a fairly good supply of blood vessels reach the skin, though not to the same extent as in the frog. This is contrary to the general belief that the dry skin of the reptiles and birds is not respiratory. What Walter says below is typical of the belief on the subject: "The reptiles as a group are definitely committed to life on land, in spite of certain backsliding exceptions, and this fact has left its modifying impress upon the skin, which is no longer thin, moist and respiratory, but thick and cornified against exposure to dry air."

The output of carbon dioxide through the skin of the pigeon is 7.6% of that given out through the lungs. The skin of the pigeon is thinner than that of Calotes and is not supplied with blood to the same extent. This animal therefore uses its skin for respiratory purposes only to a limited extent.

Among the mammals there is possibility of diffusion through the epidermis as well as evaporation through the secretions of glands when they are present. The amount of carbon dioxide thus given out through the skin in man has been found by Giuseppi Franchini and Luigi Preti to be 1% of the pulmonary output. The corresponding figure for the bat is 35%. This high figure is due to the large amount given out through the vast expanse of the patagium by diffusion. In the rabbit it is 7.6%. These figures indicate that man uses his skin to a much less extent for carbon dioxide elimination than the other air-breathing vertebrates tested (Calotes, pigeon, bat and rabbit).

By taking into account the total surface area of the animals, the above figures can be utilised to estimate the output of carbon dioxide for a certain area. Thus the amount given out from 1000 sq. centimetres of the skin in 4 hours is found to be in the frog 97.3 c.c., in Calotes 67.9 c.c., in pigeon 29.8 c.c., in man 37.0 c.c., in bat 18.1 c.c. and in cat 10 c.c. In man and rabbit, the output is through diffusion and evaporation. In the lizard Calotes, pigeon and cat it is mostly due to diffusion as there are either no glands or only a few. The greater permeability of the skin of the lizard and pigeon compared to the glandular skin of the mammals is obvious.

SUMMARY

1. The excretion of carbon dioxide through the skin of the frog when at rest is 225% of that through the lungs, in Calotes 85%, in pigeon 7.6%, in man 1%, in bat 35% and in rabbit 7.6%. Appreciable quantities of that gas are therefore eliminated through the skin.

2. The volume of carbon dioxide excreted through an area of 1000 sq. cms. of the skin in four hours in the frog is 97.3 c.c., in Calotes 67.9 c.c., in the pigeon 29.8 c.c., in man 37.0 c.c., in bat 18.1 c.c. and in cat 10 c.c.

3. Two modes of excretion of carbon dioxide from the skin are possible. One is through diffusion through the epidermis, and the other is through the glandular secretions in which the gas is dissolved. A factor which augments the elimination of carbon dioxide through the skin is its blood supply.

4. Among the animals experimented on, the least output of carbon dioxide through the skin is in the cat as it excretes only 10 c.c. in 4 hours from an area of 1000 sq. cms. This is naturally expected as the epidermis is thick and sweat glands are absent except on the paws.

5. Next comes the bat with 18.1 c.c. per 1000 sq. cm. in 4 hours. This is also not surprising since the bat offers a large surface for diffusion in its patagium.

6. The corresponding figure for pigeon which comes next is 29.8 c.c. This high amount of output is possible as the epidermis is thin.

7. Next in the scale comes man with 37.0 c.c. This is mainly due to the large number of sweat glands though the epidermis is comparatively thick.

8. Calotes ranks next as it can eliminate 67.9 c.c. This high figure is the result of comparatively thin epidermis, and the tolerably good blood supply of the skin.

9. The frog which tops the list with 97.3 c.c. has a thin and glandular epidermis which is richly supplied with blood, from below.

10. The general belief that the skin is no longer respiratory in the reptiles as it is dry is not borne out by the experiments on Calotes. On the contrary it is shown that it plays a very significant part as it excretes 67.9 c.c. per 1000 sq. cms. in 4 hours against 97.3 c.c. in the frog. This is natural since lizards come next as representatives of reptiles in the evolutionary scale.

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A STUDY OF FISH EGGS AND LARVAE FROM MANX WATERS

I. Observations on the Fish Eggs

By

DR. D. V. BAL, M.SC., PH. D. (L'POOL),

Department of Zoology, Royal Institute of Science, Bombay

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INTRODUCTION

THE fish eggs and larvæ—important constituents of plankton from the fisheries point of view, have been widely studied in different waters for many years past. However no work on the subject has been so far done in Bombay, although a large number of edible fishes is found along the Bombay coast. The writer was therefore advised to go to a place like Liverpool and to get himself interested in this kind of work.

The University of Liverpool has a department of Oceanography and also a Marine Biological Station at Port Erin, Isle of Man. Here the plankton in general of the Irish Sea to south-west of the Isle of Man has been intensively studied over a number of years by Herdman, Scott, Johnstone and others. But the fish eggs and larvæ have not received sufficient attention, apparently due to the extensive nature of the work.

It was therefore suggested to the writer by Dr. R. J. Daniel, D.Sc., the then Director of the Port Erin Biological Station, to undertake a systematic investigation of fish eggs and larvæ of the Manx Waters in the vicinity of Port Erin. Accordingly this work was carried out for about two years 1939-40. Some of these observations have been published in England (Bal 1940 and 1941), and the rest is being published in this Journal partly due to war and partly due to its general interest.

I am greatly indebted to Dr. R. J. Daniel, D.Sc., Lecturer in Fisheries, University of Liverpool, for his ever willing help and advice during the course of these studies. I should like to thank Mr. W. C. Smith, Curator, Port Erin Biological Station, for his kind assistance in the collection of the material, and also the authorities of the University of Bombay for awarding to me the Sir Mangaldas Nathubhai Technical Scholarship for work in fisheries.

AREA OF INVESTIGATION

The area investigated lies between the south-west coast of the Isle of Man and two miles off-shore and is continuous along the coast for nearly four miles. It lies outside the entrance to Port Erin Bay, but the bay itself is also included. If Bradda Head, on the north side of the entrance to the bay, is taken as centre, an area of two miles radius includes the positions of practically every haul.

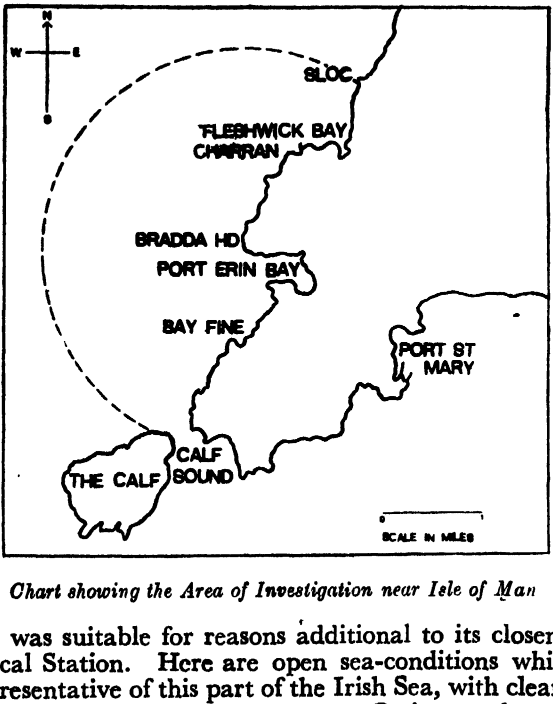


Chart showing the Area of Investigation near Isle of Man

This area was suitable for reasons additional to its closeness to Port Erin Biological Station. Here are open sea-conditions which may be taken as representative of this part of the Irish Sea, with clear water and depths favourable for spawning purposes. Owing to the proximity of land, however, the tidal streams run more fiercely in this region than outside, and as a result large masses of water move in and out on the flood and ebb tides, carrying with them fish eggs and young from beyond the particular area under survey. Proximity to the shore is equally important because the eggs and larvæ of shore fishes appear in their due season to augment the population.

It may be noted in this connection that the harbour at Port Erin dries out at each tide. The motor boat was used as soon as she was afloat, so that the collections were taken at different hours of the day but at approximately the same state of the tide, when the flood was well made and a large mass of water had invaded the area. The eggs and larvæ under discussion, therefore, may have the added value of being augmented from a wider region.

APPARATUS

Two nets were used in the present investigations :—

1) A Young-Fish Trawl.
2) A Surface Tow Net.

The young-fish trawl was made exactly half the size of the Plymouth young-fish trawl (Clark 1920), using stramin for the mesh work. This was because it was necessary to regulate the size of the nets to that of the motor boat available for the working of them.

The advantage of having a young-fish trawl with half the catching capacity of the Plymouth model lies in the fact that, if necessary, direct comparison may be made of catches from a quantitative point of view. The efficacy of the young-fish trawl as a quantitative net has been discussed by Gardiner and Graham (1925).

The surface net, made of No. 9xx silk bolting cloth, had the following dimensions :

Diameter of Ring	24 inches
Length of Canvas Top	31 ,,
Length of Silk Bag	51 ,,

The surface net, thus, had 1/3 of the catching area of the fish trawl, although the coefficient of filtration in the two nets was not the same owing to the differences of mesh in the materials used. The nets were as far as possible towed at a constant speed and usually, excepting on one or two occasions, for fifteen minutes.

The young-fish trawl was operated on all but one occasion outside Port Erin Bay and the surface net was used along with it for certain hauls. The latter net was also used frequently inside the shallow waters of the bay when the state of the tide permitted in order to detect any differences in the distribution of eggs inside the bay and outside.

The fish trawl was actually used at different depths of water by paying out various lengths of warp between 18 to 90 metres. In the absence of a depth finder, the distance of the net below the surface for various lengths of warp was found out in the following manner.

A light line was fastened to the mouth of the net and suspended from a small boat which, by keeping pace with the towing boat, kept the measuring line as vertical as possible. It was possible in this way to ascertain by trial the different depths at which the net was fishing. The rate of towing was always kept as constant as possible, and the following table gives the amount of warp out and the corresponding fishing depths.

Length of Warp in metres		*Fishing Depths in metres*
18	..	4·5
27	..	5
36	..	5·4
45	..	5·8
54	..	6.3
63	..	6.6
72	..	6.8
90	..	7·2

The depths given for 27, 45 and 63 metres of warp in the above table have been obtained by interpolation ; each one is referred to only once in the text.

MATERIAL AND METHODS

The material consisting of 24,735 fish eggs was obtained from samples, taken once or more a week, weather and other conditions permitting, for a period of about eleven months, beginning in February and ending in December 1939.

72 out of a total of 95 hauls with the young-fish trawl contained fish eggs or larvae or both ; similarly 45 out of 56 hauls with the surface net turned out to be successful and 14 of them were from Port Erin Bay. Most of the samples from October onwards were lacking in fish-eggs and larvae.

Some of the eggs, while fresh, were hurriedly sorted out in the laboratory under a binocular microscope and placed in plunger jars. The larvae hatched from them were reared until they had developed some distinguishing features, useful for the identification of the species. The rest of the material was fixed in formalin and was subsequently studied at Port Erin Biological Station and at the Department of Oceanography, Liverpool University.

Some of the large number of preserved eggs were measured under the microscope by means of a micrometer eye-piece and their diameters are expressed below in millimetres.

It is proposed here to deal in detail with the eggs taken with the young-fish trawl, species by species, and then to add for each species a short account based on observations of the surface net catches.

The order of the species followed in this paper is according to the Fauna Ichthyologique de L'Atlantique Nord, 1938.

THE FISH EGGS

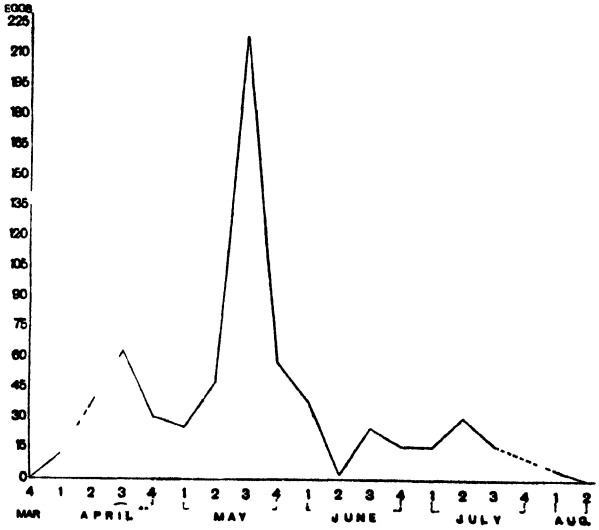
1. *Clupea sprattus* (L)—Sprat

YOUNG-FISH TRAWL

More than 2,000 sprat eggs were taken at depths of 4.5 to 7 metres as a result of fifty-four drags with the half-sized young-fish trawl during the season April to August 1939. They occurred regularly in the samples and were placed second in the numbers recorded for the various species of eggs taken by this trawl. It is apparent that sprat eggs are more abundant in the Manx waters than could be expected from the scanty references to them made in past reports.

The eggs of this fish are readily recognised because they are not truly spherical, a fact already noted by Buchanan-Wollaston (1911). The segmented nature of the yolk is equally characteristic and is plain in fresh and also in preserved eggs, in which the cleavage has begun. The eggs capsule is thin, enclosing white and transparent yolk. The larger sized sprat eggs may occasionally be confused with small whiting eggs, but the yolk of the latter is yellowish and vacuolated. They can also be distinguished from large dab eggs by not being truly spherical. The present identifications of sprat eggs were confirmed by hatching out a number of them in plunger jars.

The eggs were first obtained at the beginning of April and were then found in all the samples until the end of the first week in August. The spawning period, therefore, extends over five months or more; Robertson (1938) gives an account of spawning times in other areas. In Manx waters the number of sprat eggs was highest in May (see table 1) and the figures of weekly averages show the peak of the spawning to be during the third week of that month. Smaller fluctuations in the average numbers reflect the irregularities of the hauls frôm week to week.



Graph of Weekly Occurrence of Sprat Eggs in 1939

Average Number of Eggs per Haul Week by Week.

Week	April	May	June	July	August
I	11.5	25.1	38.6	16.5	5.2
II	....	48.3	2	31	0
III	63.5	219.3	25.7	17.3	0
IV	31	58.6	16.6	..	0

Some eggs from each haul were measured in order to find the variations in dimensions throughout the whole season. The minimum and maximum diameter of sprat eggs was thus 0.80 and 1.06 mm. respectively. It is not necessary to give here the diameter of every egg measured from each sample, instead it will be sufficient to state only the average diameter for the following months of the spawning period.

Month	Average Diameter in mm.
April	0.98
May	0.95
June	0.91
July	0.89

The above figures show that the average diameter is less as the spawning advances.

SURFACE NET

There were 998 sprat eggs in thirty surface net samples, eight of which were from Port Erin Bay. The eggs were found, therefore, both inside and outside the Bay, which is a further evidence of their abundance around Port Erin. These catches with the surface net, as well as those taken at greater depths with the young-fish trawl, show that sprat eggs are distributed in the upper as well as the lower layers of water, which agrees with the findings of F. S. Russell (March 1926) at Plymouth.

Eggs appeared first in the surface net in the last week of March, that is, earlier than in the fish-trawl; but they ceased to occur in both nets early in August and the spawning time may, therefore, be stated as March to August.

In the hauls of both nets the numbess of eggs taken were liable to fluctuations and at one period, the third week in April, the surface net obtained its biggest haul. It is not considered, however, that this is the peak of the spawning, because after this period the catches are more equable and show a steady rise to May which is to be regarded as the true maximum. The disconcerting irregularities at the beginning of the spawning season are probably due to fortuitous circumstances which have concentrated the eggs at certain times.

The diameter of the eggs ranges between 0.81 to 1.22 mm., and thus the variation is higher than stated for the young-fish trawl. Ehrenbaum (1905—09) gives 0.82 to 1.23 mm. as the size of eggs from the North Sea.

2. Argentina sphyraena (L)—Lesser Silver Smelt

YOUNG-FISH TRAWL

This species is not uncommon in British waters, but its eggs do not seem to have been recorded from the Irish Sea. The eight eggs reported here have, therefore, a special interest.

These pelagic eggs are comparatively large, and so is the contained oil globule which is almost colourless, but it appears yellowish or pink when preserved. The yolk is made up of numerous cell-like vesicles which are similar to those found in Clupeoid eggs. It is possible, therefore, to confuse the egg of this species with that of the pilchard; but this can be avoided by a glance at the size of the oil globule which is more tha twice the size of that in the pilchard egg. In addition the egg capsule bears very fine hair-like striations

The eggs under discussion were obtained from six different hauls of the fish-trawl at depths stated below, but none was present in corresponding surface net samples. It may therefore be argued that they float a little below the surface, which might account for the absence of past records in this area. The first egg occurred on 6th of April and the remaining seven during the month of May. The spawning thus seems to take place during April and May, probably even earlier, for well-developed ovaries were found in two specimens of *A. sphyraena*, caught in the month of February, and preserved in Port Erin Museum.

The diameter of the eggs and oil globule varies between 1.70 to 1.84 mm. and 0.40 to 0.45 mm. and thus the oil globule is less than one-fourth of the size of the egg. The full details of the eggs are as under :—

Date	Depth in metres	No.	Diameter of Egg in mm.	Diameter of Oil Globule in mm.
6-4-39	..	1	1.84	0.41
3-5-39	6.8	1	1.81	0.43
8-5-39	4,5	3	1.80	0.40
10-5-39	4.5	1	1.70	0.45
18-5-39	4.5	1	1.70	Not clear
20-5-39	4.5	1	1.76	,,

Two of them were put in the plunger jar and the hatched larvae resembled those of *A. sphyraena* in every respect. Their elongated body characterised by the black pigment patches as figured by Johs Schmidt (1906). One of them was for a short time removed from the jar for the sake of identification and measurement, but it died some hours after being returned to the jar. It was then found to have lost about 2 mm. of its original length of 9 mm., which is an interesting reflection upon the amount of shrinkage that takes place in larvae after death. The other larva was killed before the complete absorption of the yolk-sac for purposes of record.

3. Gadus callarias (L)—Cod

YOUNG-FISH TRAWL

The cod, being a very common fish in this district, forms an important fishery in the winter in the vicinity of Port Erin. Its eggs, also found in large numbers, are third in order of abundance in our fish trawl records. The abundance of their occurrence is, in addition, proved by the presence of the many larval and post-larval stages in these samples from April to June.

The cod eggs can be identified by their large size and thick yellow yolk. Kramp (1913) stated that cod eggs have a non-iridescent pellicula and the description is applicable to those from Manx waters. The egg capsule is, moreover, thick, although not so much as that of the plaice. The eggs containing embryos are easily recognised because the latter have characteristic black pigment patches. Many of them were hatched in plunger jars in order to verify the identification.

There appeared in these collections some lemon-sole eggs at the beginning of May and there was an occasional difficulty in separating the two by size alone. Lemon-sole eggs, however, unlike those of cod, have striations on the capsule which form a distinguishing feature. Some whiting eggs, also, are similar in size to cod eggs, although the former unlike the latter contain loose vacuolated and pale yellow yolk.

1,305 cod eggs were obtained between February 10th and May 18th and accordingly the spawning time was longer this season than has been recorded previously for Manx waters. The following weekly averages show that the number of eggs is high at the end of March and is abundant during the third week in April. It falls suddenly after this date and there were no records after the third week of May.

Average Number of Eggs per Haul Week by Week

Week	February	March	April	May
I	0	6	59.5	23.8
II	1	14	..	15.3
III	..	..	*341*	1.3
IV	18	214	6	0

The diameter of the eggs varies between 1.15 and 1.58 mm., which nearly agrees with that of lemon-sole eggs. The average diameter, month by month, is as under, although the figure for February is obtained from few eggs.

Month	Average Diameter in mm.
February	1.49
March	1.47
April	1.40
May	1.28

SURFACE NET

1,415 cod eggs were taken with the surface net and this number is proportionately bigger than that recorded with the young fish trawl. Their regular occurrence in both the nets shows that they are generally distributed in this water but nearer to the surface, and that they are common inside the bay, though more so in the open area outside it.

The weekly average figures (see table IV) fluctuate at intervals and reach their maximum some time in the third week of April as in the other net. The average for the second week in March, when cod eggs first appeared in the surface net, is unusually high and may be attributed to a sudden influx of cod eggs into the bay due to inshore winds.

The largest egg measured being 1.60 mm. in this case, the range of variation in size may be stated as 1.15—1.60 mm.

4. **Gadus minutus**, O. Fr. Muller—Poor cod

SURFACE NET

Herdman (1902) states that this species occurs in our district, but it is not included in the Marine Fauna of the Isle of Man (1937). A. Scott (1913) wrote that the eggs of the poor-cod were certainly represented in the plankton from the south-west of Man, although he only separated them from those of green-cod, bib and certain other gadoids provisionally. This and such other records indicate the presence of the poor-cod eggs in this neighbourhood.

It is a well known fact that some gadoid eggs overlap in their sizes and are thus difficult to distinguish with certainty. At the same time it seems possible to identify many of them by comparison of their diameters. The diameter of 299 eggs under consideration varies between 0.90 to 1.06 mm. which is within the range of a gadoid, having small sized eggs. Ehrenbaum (1905—09) gave 0.95 to 1.07 mm. as the range of size of the poor-cod eggs, and Hefford (1910) 0.91 to 1.02 as the size of eleven eggs taken from a ripe female. The above eggs, therefore, have been identified as those of the poor-cod. The smaller whiting eggs approach in size to the larger poor-cod eggs; but there is not much possibility of confusion here since such whiting eggs are very few in March and April, the time of occurrence of these eggs.

The above eggs were obtained from twelve surface net samples, both from inside and outside Port Erin Bay. They were found first on March 9th and last on April 18th, and thus the period of occurrence seems to have been short during 1939. Their average diameter for March—April was approximately 0.98 mm.

5. **Gadus merlangus** (L)—Whiting

Young-Fish Trawl

Whiting eggs were plentiful and numerically highest amongst the eggs of the different species found in the young-fish trawl hauls.

They may be identified with the help of the egg-capsule, appearance of yolk and by size. The egg-capsule is thinner than that of the cod egg and if examined minutely is found to be slightly rough. The yolk is vacuolated and the small vesicles are distinctly visible in eggs containing embryos, in which case they are easily distinguished from the eggs of allied species. The size of the egg is likewise useful in identification, although not so important as the other two characters. It has been stated in literature that occasionally there is a difficulty in separating with certainty some whiting eggs from those of the other gadoids, owing to overlapping in size, and certainly confusion may arise when size alone is considered. The present identifications were checked, however, by hatching out a large number of eggs in plunger jars.

Whiting eggs are so common in the collections that their number amounts to 4,814, out of which 1,493 occurred in one drag alone. They first appeared on February 10th and then continued to do so almost regularly up to the first week in June. The number of eggs rose at the end of March and was abundant for about three weeks in April. It remained fairly high in the first half of May and then completely disappeared early in June. The spawning period of the whiting, therefore, lasts over five months—February to June.

In addition the following figures of weekly averages indicate that the actual peak of the spawning falls somewhere in the first week of April. This peak is probably maintained during the following week but unfortunately no haul could be taken at that time. However, the average number in the third week of the month is still very high and may be regarded as continuous with the early April maximum.

Average Number of Eggs per Haul Week by Week

Week	February	March	April	May	June
I	0	21	837	80.8	2
II	15	63	..	90.1	0
III	..	..	752	7.6	0
IV	66	242	55	8	0

Many eggs were measured and the measurements show that the diameter of whiting eggs varies between 0.96 to 1.33 mm. which is nearly the same as 0.97 to 1.32 mm. quoted by Ehrenbaum (1905—09) for the North Sea. The average diameter during months of the spawning season is as follows :—

Month	Average Diameter in mm.
February	1.21
March	1.14
April	1.12
May	1.06

The average for February is calculated from only two hauls of few eggs and none is stated for June, since only six eggs were taken in that month.

SURFACE NET

The number of whiting eggs obtained by this net was 3,072 which is second in order of total abundance. Their abundance in the fish trawl proves, in addition, that they are most common in this area and that they are distributed in different layers of water fished through, although in the greatest numbers near the surface. It may be noted in passing that the eggs are usually found both inside and outside the bay.

The average number of eggs in the first and third weeks of April is again very high, which, therefore, agrees with the findings of the fish trawl. There is, however, an exceptionally high average for the second week in March and this irregularity, as already explained for cod eggs, is an effect of a sudden concentration of eggs within the bay.

6. **Molva molva** (L)—Ling

YOUNG-FISH TRAWL

The common ling is an important commercial fish, and is common to the West of the British Isles. Its larval and post-larval stages are also well known. There seems to be no record of its eggs, however, although they were mentioned in the last century by McIntosh and Prince, and Holt. A. Scott (1913) has recorded a single egg of *M. vulgaris* Flem. on 27th April 1908 in Manx waters.

It is, therefore, important to record 176 ling eggs in one season. The eggs, though small, contain a large pale-green oil globule, about one fourth of their size. The egg-capsule is thick, appearing as if made up of two layers—an inner and an outer, as figured by McIntosh and Masterman (1897). The eggs of turbot nearly approach these eggs in size and are often found in the same samples, but they can be separated by means of the oil globule which is much smaller than that of the ling.

Some of them had embryos, having almost a regular double line of black chromatophores along the back as described by Ehrenbaum

(1905—09). Such eggs also have black chromatophores on the oil globule and a few scattered in the yolk, and thus the pigmented embryos are useful for identification purposes. The remaining eggs appear to have been freshly spawned and the question therefore arises as to where this spawning took place. It is generally held that ling favour water 90—200 metres for this act; see, for instance, Meek (1916) and Howell (1921). Now such depths of water in the northern part of the Irish Sea are only found over a channel, the eastern edge of which, with a depth of 108 metres, lies ten miles to the west of Port Erin Bay.

Two ling eggs occurred first on the 18th of April and others continued to appear in small numbers up to the 23rd of August. The spawning period, thus, extends from April to August, which appears to be longer than that given for previous British records. Meek (1916), however, writes that "Spawning also takes place at the Faroes, and to a large extent west of Scotland in April, May and June, and the season may extend into July or August. This is also the case for the west of Ireland, as Holt stated." It will be seen from Table I that more eggs are found in Manx waters during July and August than in the earlier months of the spawning season. In addition, the figures of the weekly averages indicate that the peak of the spawning is reached during the third week in July and that the average for the first week of August is fairly high. It can be inferred from the material in hand that the spawning is high during these weeks and then falls away. It is more usual for spawning to be most intense at or near the middle of the spawning period. This is certainly the case with the majority of species that spawn in these waters and it may be argued that the influx of ling eggs towards the end of the spawning season was due to a drift into our area from some neighbouring ground. In that case the ling may be spawning some distance from Port Erin, at greater depths than are found in the coastal area under examination.

Average Number of Eggs per Haul Week by Week.

Week	April	May	June	July	August
I	0	0.6	0	11	12.4
II	..	0.5	0	1.5	2
III	1	0.6	5.2	13.3	..
IV	0.5	0.7	0.4	..	0.4

The diameter of the eggs and the oil-globule lies between 0.96 and 1.09 mm., and 0.27 and 0.32 mm. respectively. These dimensions are nearly the same as those given by Ehrenbaum (1905—09) for the North Sea eggs, but those quoted by some workers for specimens from near British coasts range between 1.07 and 1.10 mm. for the eggs, and 0.30 and 0.40 mm. for the oil globule.

There are few eggs to be measured, some hauls containing only one egg; the following monthly average diameters are, therefore, approximate and subject to some alteration.

Month	Average Diameter in mm.
April	1.04
May	1.03
June	1 03
July	1.01
August	1.00

SURFACE NET

Twelve ling eggs (see Table II) occurred in six surface net samples, one of which was from the bay. The evidence from the catches with the fish trawl tends to show that the ling eggs are taken in greater numbers just below the water surface, and that may account for their poor number in this net. It may even explain the cause of their absence from past Manx records, which were mostly taken with the surface net.

7. **Onos mustela** (L)—The Five Bearded Rockling

YOUNG-FISH TRAWL

Rockling eggs, which are very common in this area, occur over a period of seven months. The majority of them are referred to *O. mustela* and only a few to *O. cimbrius* as discussed below.

It was found that from June onwards there occurred two distinct kinds of rockling eggs—one consisting of slightly larger eggs with a correspondingly large oil globule, and the other vice versa. The former seem to belong to *O. cimbrius* and the latter to *O. mustela* as the dimensions of the egg and oil globule of the four bearded rockling appear to be greater than those of the five bearded rockling for corresponding months of the spawning period.

The eggs of the five bearded rockling are usually recognised by means of their size, oil globule and egg-capsule as already described by other workers. The corrugated look of the latter is especially useful in differentiating them from the eggs of the Norwegian Top-knot (S. norwegicus, Gunther) and the Rainbow Wrasse (*C. julis, L.*), because in other respect the eggs of these three species are not very dissimilar. The size of the oil globule is also helpful in separating the eggs of this species from those of the Four Bearded Rockling and, to some extent, from those of the Norwegian Top-knot.

O. mustela eggs have been recorded previously from January onwards but in the present season no hauls were taken in January, and only three in February, which had no rockling eggs. They were here noted first in a drag on March 3rd and last on September 22nd; and were taken regularly in every haul during March, April and May, and at intervals from June to September. This species has, therefore, a much more extended spawning period than the majority of other fish, lasting over seven months or more (see Table I).

The occurrence of these 380 eggs is rather irregular and hence it is not possible to note with certainty the time of the maximum spawning from the weekly averages given below. It can, however, be reliably said that the spawning is intense in March and April, and this is further supported by the figures for the surface net (see Tables II and IV).

Average Number of Eggs per Haul Week by Week

Week	March	April	May	June	July	Aug.	Sept.
I	37	9.5	5	8.6	0.5	1.2	0.5
II	2	..	10.6	1	2	0	..
III	..	23.5	4	3.5	0.3	..	0
IV	28	7.5	8.7	0.2	..	0	0.2

The size of *O. mustela* egg and of the oil globule ranges between 0.66 and 0.91 mm. and 0.12 and 0.19 mm. The average monthly diameter of the eggs, excepting months with only few eggs, is as follows :—

Month	Average Diameter in mm.
March	0.80
April	0.80
May	0.78
June	0.73

SURFACE NET

5818 *O. mustela* eggs, being first in order of abundance, were obtained with the surface net, although only 380 were recorded with the fish-trawl. These numbers clearly point out that the rockling eggs are commoner at or near the surface than in the deeper layer of water. A comparison of individual hauls reveals, furthermore, that the eggs occur in greater number in the bay than in the area outside it. Probably this is due to the rocklings spawning inside the bay itself and in this way augmenting any supply of eggs that may be carried in.

The diameter of the eggs varies between 0.64 and 0.98 mm., the maximum being thus greater than stated above. It may be added here, that occasionally some eggs instead of having one oil globule, contain two or three.

8. Onos cimbrius (L)—The Four Bearded Rockling

YOUNG-FISH TRAWL

Holt (1897—99) speaks of "the undoubted existence in the district (i. e. Plymouth), of *M. cimbria*" and Herdman (1902) writes "It probably extends up the Irish Sea." These and other such notes establish the presence of this species in British waters including the Irish Sea. In addition a small number of *O. cimbrius* eggs, of which there is no previous record from Manx waters, have been obtained in the present samples. This absence of past records is probably due to the great similarity there is between the eggs of *O. cimbrius* and those of *O. mustela*, which has led them to be overlooked or misidentified.

As already pointed out there occur from June onwards few rockling eggs other than those of *O. mustela* and they belong either to *O. cimbrius* or *O. tricirratus*. The latter species is noted in Manx waters but it need not be considered further in the present connection if its spawning period —November to January—as stated by McIntosh and Masterman (1897) is reliable and also if its oil globule is as large as 0.22 mm. This evidence shows that the eggs under consideration belong to *O. cimbrius*, which is also confirmed by the hatched larvae.

50 eggs of the four bearded rockling were found in sixteen drags of the young-fish trawl from June to September. The spawning period of this species, probably commencing later than that of *O. mustela*, extends from June to September or so in this area. Clark (1920) has also recorded a ripe female on 2nd September 1913, at Plymouth, which gives additional support to the above view about the spawning time.

As stated above there is a great similarity between the eggs of the two rocklings, although the egg-capsule of *O. cimbrius* seems to be less corrugated than that of *O. mustela*. The diameter of the egg and oil globule varies betwen 0.75 and 0.87 mm. and 0.16 to 0.18 mm. respectively. The range of variation is limited but more material needs to be examined before drawing any definite conclusion about the size. It may, however, be added that the monthly average diameter of *O. cimbrius* eggs is rather higher than the corresponding one of *O. mustela*.

Month	Average Diameter in mm.
June	0.82
July	0.81
August	0.81

SURFACE NET

11 eggs of the four bearded rockling were taken from five surface net samples from June to August. The small number of eggs in both nets shows the general scarcity of this fish in the area under review.

The dimensions of these eggs and the oil globule vary between 0.80 and 0.86 mm. and 0.16 to 0.19 mm.

9. **Coris julis** (L)—Rainbow Wrasse

YOUNG-FISH TRAWL

The Rainbow Wrasse is recorded in the Marine Fauna of the Isle of Man, but there is no mention of its pelagic eggs. The latter are apparently scarce in this locality as only 5 eggs were secured from two hauls taken in August 1939.

Holt (1891) has recorded "coris-like" eggs off the West coast of Ireland (diameter 0.80—0.83 mm.) and also in the Plymouth district (diameter 0.78—0.81 mm.) These measurements are somewhat greater than given by Raffaele and Holt (1897—99) (diameter 0.58—0.70 mm.) for the eggs of Mediterranean specimens of *Coris julis*, whereas the size of the eggs under consideration is within the range quoted for the Mediterranean and may be identified with certainty as belonging to this species.

The Rainbow Wrasse eggs are somewhat similar in appearance to the smallest-sized eggs of *O. mustela* but they cannot be confused with them because careful examination reveals that, unlike in *O. mustela*, the egg-capsule is non-corrugated and without an air vesicle.

The diameter of the eggs is 0.61 to 0.65 mm. and of the oil globule 0.15 to 0.18 mm.

SURFACE NET

Only 3 eggs, one in each of the months May, June and July were obtained from the surface net. Together with the catches in the young-fish trawl this shows a rare occurrence of the eggs in the area under investigation.

The oil globule was 0.12 mm. in diameter in two cases, and in the third it was misshapen.

10. **Ctenolabrus rupestris** (L)—Jago's Goldsinny

YOUNG-FISH TRAWL

The eggs of this variety of Wrasse have been noted in small numbers from the South-west coast of Ireland by Holt (1891) and from Manx waters by A. Scott (1913), but according to Hefford (1910) they seem to be numerous around Plymouth. In the present case 46 eggs are recorded from thirteen hauls with the young-fish trawl.

These eggs are small and without any oil globule, and thus not very difficult to distinguish, particularly as they occur during the later part of the summer when other eggs that might possibly be confused with them are not present. They are more easily recognised when the pigmented embryo is formed because the latter has black spots arranged regularly in a row on each side of the body.

The eggs were noted first on August 1st, and last on October 12th. Forty-three of them occurred in August, two in September and only one in October.

Their diameters range between 0.91 and 1.06 mm. which means the maximum size is slightly higher than in previous records. Ehrenbaum (1905-09), however, has already anticipated a bigger diameter for eggs in the south of Britain, and Hefford (1910) also writes that the size of these eggs is liable to much variation. The maximum diameter stated by Holt (1897-99) is 1.01 mm., but ten of the present eggs were higher than this as shown below.

No. of Eggs	Diameter in mm.
1	1.06
1	1.04
4	1.03
3	1.02
1	1.015

The rest of the eggs were 1.01 mm. or below that in size and the average diameter for August was 0.98 mm.

SURFACE NET

10 *C. rupestris* eggs were found in three surface net samples, taken outside the bay in August. Their diameter was 0.79 to 1.02 mm. and the minimum was thus lower than recorded above under the young-fish trawl. The combined range of variation may, accordingly, be stated as 0.79 to 1.06 mm., while Holt (1897-99) has quoted 0.72 to 1.01 mm. for Plymouth eggs.

11. **Callionymus lyra** (L)—Dragonet

YOUNG-FISH TRAWL

The Dragonet eggs, like those of the Rockling, are very common in Manx waters and occur almost regularly over a period of about five months.

They are most easy to identify because of the presence of the characteristic almost hexagonal reticulations on the zona radiata. This and other distinguishing features have been described by other workers especially by McIntosh (1885). The reticulations are most clearly seen when part of the yolk has been absorbed. It may be added that the yolk, being very dull, gives the eggs a peculiar appearance which distinguishes them from other similar sized eggs, even before examining the reticulations under higher magnification. Many of them were hatched in the plunger jars for identification purposes.

448 *C. lyra* eggs occurred in the young-fish trawl from 22nd February to 21st June and later than this date in the surface net. A majority of them was taken in April and May, in which months the spawning must

be abundant. The following weekly averages, besides, show that the peak of the spawning lies sometimes in the third week of April, which is also the case with the catches of the surface net (see Table IV)). The number of eggs, however, continues to be fairly high during the first half of May and then falls gradually.

Average Number of Eggs per Haul Week by Week

Week	February	March	April	May	June
I	0	6	13.5	18.3	5
II	0	2	..	18	0
III	..	..	41.5	7.3	2.5
IV	1	10	2	6.2	0

The diameter of these eggs varies between 0.73 and 0.93 mm., which is in agreement with previous records. However, a single egg found on February 22nd measured about 1.02 mm. and is, therefore, distinctly bigger than the rest of the eggs. The maximum diameter of some first spawned eggs is probably higher than stated above, but the solitary example given has, in the meanwhile, been taken as an exception.

The average diameter of the eggs during the months of the spawning period is as follows :—

Month	Average Diameter in mm.
March	0.88
April	0.86
May	0.82
June	0.78

SURFACE NET

807 dragonet eggs, definitely more abundant than in the fish-trawl, were recorded in the surface net, even though the number of successful hauls was almost equal for both. This inequality in number is by no means caused by samples from the bay, because a comparison of the catches does not reveal any concentration of dragonet eggs within the bay. It, therefore, seems that the eggs of this fish are commoner near the surface than below, and are accordingly obtained in larger numbers with the surface net than with the fish-trawl.

They occurred in this case up to July 14th, and the combined spawning time may, thus, be given as February to July inclusive. Here again the catches reached a maximum in April and were high in March and May (see Table II).

Their size is 0.70 to 0.95 mm., while Hefford (1910) quotes it as 0.70 to 0.91 mm. for Plymouth eggs.

12. **Callionymus maculatus** (Rafinesque) —Spotted Dragonet

YOUNG-FISH TRAWL

The eggs of the Spotted Dragonet—adult not recorded from the Isle of Man—have been noted from Port Erin Bay once in July 1905 and 1906 respectively. Evidently the fish and its eggs are very rare in the area under review and this is also true for the 1939 season.

2 eggs, however, were secured on June 21st in a fish trawl drag from Port Erin Bay. It is no doubt difficult to distinguish them from those of *C. lyra* but it is possible after critical examination of their hexagonal meshes, which are closer than in *C. lyra*. The eggs of the former also seem smaller than those of the latter, a fact anticipated by Holt (1897-99). The diameter of both the eggs under discussion was 0.72 mm.

SURFACE NET

5 more eggs were found in five samples with this net from outside the bay in addition to two described above from the bay. They are obviously very scarce both in and outside the bay, the adult being apparently a deeper water form.

2 of the 5 eggs occurred in May and one in each of the following three months. The spawning time probably extends from May to August, in which case it spawns later than *C. lyra*. Ehrenbaum (1905-09) and Clark (1920) give June to August as the spawning period.

The size varies between 0.69 and 0.74 mm.; this range which is within that given by Ehrenbaum—0.66 mm. to 0.79 mm.—is only based on few measurements and is therefore provisional.

13. **Trigla gurnardus** (L)—Grey Gurnard

YOUNG-FISH TRAWL

The Grey Gurnard is recorded as the commonest species of gurnard in the Irish Sea and its eggs are certainly common in the samples. Many gurnard eggs are noted below and almost all of them belong to this species. In rare cases the eggs, when fresh, had a copper-coloured oil globule like that found in the Red Gurnard eggs. This colour disappeared after fixation and then it was not possible to distinguish the two types of eggs, because of their similar dimensions.

Some eggs were reared in plunger jars and the hatched larvæ were those of the grey gurnard. It was found, in addition, that the early larval and post-larval stages taken in the young-fish trawl belonged to the Grey Gurnard. It can be inferred therefore that the eggs of the Red Gurnard are rare in waters to the southwest of Man, and that here we are dealing almost exclusively with those of *T. gurnardus*.

The large eggs of *T. gurnardus* contain yellow yolk and the egg capsule is thick like that of the cod's egg. The oil globule is large and yellow, though dull yellow or smoky after preservation. Occasionally it becomes indistinct which renders the accurate measurement rather difficult. It may be that a few eggs, in which the oil globule was almost lost in the yolk, appeared at first sight to be those of the Cod, but a faint oil globule could be detected after close examination with the aid of artificial light. This obscurity seems to be due to the dense yolk and dull appearance of the oil globule in preserved condition.

379 Grey Gurnard eggs were recorded between March 24th and August 14th and thus the spawning time may be taken as March to August. They occurred almost regularly during this period and were present in all drags excepting only a few at the end of the spawning season. The number of eggs increased soon after the middle of April, and reached its maximum by about the middle of May. Numbers on the whole remained high until about the end of June and then depreciated. The general nature of their occurrences this season is shown by the following weekly average figures.

Average Number of Eggs per Haul Week by Week

Week	March	April	May	June	July	August
I	0	1	4.1	8.3	1.3	2
II	0	..	17.3	1	4	0.3
III	..	14	3.7	12.5	2.6	..
IV	1	5	11.1	0.6	..	0

The size of the eggs and oil globule is 1.17 to 1.61 mm. and 0.19 to 0.34 mm., and this range of diameter is a little higher than the previous British records. It is probably a result of extensive study carried on for the whole of the spawning period. Ehrenbaum (1905-09), however, gives almost similar dimensions for the North Sea eggs of the Grey Gurnard.

The average monthly diameter of the eggs are as under :—

Month	Average Diameter in mm.
April	1.48
May	1.43
June	1.38
July	1.29
August	1.23

SURFACE NET

The surface net took only 29 Grey Gurnard eggs, out of which two were from Port Erin bay. The inequality in the catch of the two nets shows that they are not only less common inside the bay but also at the surface of the water. It was noticed, moreover, that they occurred in this net only between April 18th and June 17th which is nearly half the catching period of the fish trawl. The spawning is undoubtedly continued beyond June, but the surface net fails to catch the eggs, because they probably float below its fishing depth.

14. **Rhombus maximus** (L)—Turbot

YOUNG-FISH TRAWL

Turbots are not uncommon around the Isle of Man and the writer was able to collect some young turbots with a push-net close to the shore in Port Erin Bay. There are, however, only meagre records of turbot eggs in the vicinity of Port Erin and these date back to 1903-1906 and 1913. The present samples contain 44 turbot eggs and these may be considered an important addition to the records. A few of them were placed into plunger jars and hatched out successfully.

Turbot eggs are medium sized and contain an oil globule. The capsule has a few wrinkles but these are not so distinct as described by McIntosh (1895). Some of the eggs are similar in diameter to Ling eggs but the contained oil globule is smaller. Sometimes a turbot and a Muller's Top-knot egg have nearly similar dimensions including that of the oil globule but the latter egg is devoid of any wrinkles on the capsule.

The eggs were collected between May 29th and September 6th, though mainly in June and July. They have, however, been recorded in April and thus the spawning time may be noted as April to September. The material in hand is so very scanty that it is not possible to arrive at any further conclusions about spawning from the following weekly averages.

Average Number of Eggs per Haul Week by Week

Week	May	June	July	August	September
I	0	0.7	2	1	0.5
II	0	0	2.5	0.7	..
III	0	2.2	2.3	..	0
IV	0.7	0.6	..	0	0

The minimum and maximum size of the eggs and oil globule are 0.94 to 1.09 mm. and 0.15 to 0.21 mm. respectively. This range of variation is more than previous records for British eggs and slightly less than that for North Sea eggs. Average diameters in the present case are as follows:

Month	Average Diameter in mm.
June	1.05
July	0.99
August	0.98

SURFACE NET

The surface net caught only 1 turbot egg, on August 7th, which confirms the scarcity of this form.

15. **Scophthalmus norwegicus** (Gunther)—Norwegian Top-knot

YOUNG-FISH TRAWL

The Norwegian Top-knot, although recorded several times from the Irish Sea, is noted from Manx waters only as single records in 1896 and 1939. Likewise eggs, identified as belonging to this top-knot, were occasionally found in or outside Port Erin Bay between 1903 and 1905. It is, thus, interesting to record here 23 eggs of this fish, which is apparently not so common in our area. Some eggs were hatched out in plunger jars and the larvæ possessed a fine net-work of reticulations on their body which was covered with small diffused dots of pigment unlike the stripes of Muller's Top-knot.

The egg of the Norwegian Top-knot is smaller than that of Muller's Top-knot and the two can be separated without any doubt. It is nevertheless difficult to distinguish it from a rockling egg without resorting to close microscopical examination as stated earlier in these pages. It may be added that the oil globule in the Norwegian Top-knot egg is usually small and greenish-yellow in appearance.

These eggs, which include four from the bay, were obtained between May 29th and August 23rd. Clark (1920) gives March to June as its spawning period at Plymouth where the Norwegian Top-knots occur in abundance. The spawning extends into August in our area and the fish may, therefore, have a longer spawning time than previously recorded.

The size of the egg and oil globule is 0.74 to 0.88 mm. and 0.9 to 0.16 mm., which is nearly the same as found in other areas. The dimensions of the eggs and oil globule during the spawning season are as under.

Month	Diameter of Egg in mm.	Diameter of Oil Globule in mm.
May	0.80—0.88	0.09—0.14
June	0.74—0.85	0.10—0.16
July	0.79—0.81	0.10—0.14
August	0.79—0.84	0.14—0.16

SURFACE NET

Only one Norwegian Top-knot egg was secured with the surface, net on April 26th, and the combined spawning period may, therefore, be stated as April to August in Manx waters.

16. **Zeugopterus punctatus** (Bloch)—Muller's Top-knot

YOUNG-FISH TRAWL

Herdman (1902) writes that "it is the commonest of the little 'Top-knot's in our seas" but it is noted as not common in the Marine Fauna of the Isle of Man. A. Scott (1913) states that "the pelagic eggs of one of the top-knots, which is probably the above species, are occasionally met with in the plankton from the southwest area of the Isle of Man between April 1st and July 1st." It is thus clear that the eggs of this species have been considered as not common in this area, neither have the identifications always been definite. It may be stated, on the contrary, that numbers of eggs belonging to Muller's Top-knot occur in these samples, taken with both nets. After identification some of them were placed in plunger jars and the larvæ hatched out undoubtedly belonged to *Z. punctatus.*

The eggs of Muller's Top-knot are medium-sized with a single oil globule. Their yolk and the oil-globule exhibit a rather dull appearance, especially after fixation. Sometimes their dimensions may be similar to those of the ling or the turbot, although the differentiation can be made with the help of characters discussed under the respective heads.

292 eggs were obtained from catches taken between March 24th and June 21st. The spawning period is thus March to June in this area, but Clark (1920) quotes it as February to May in the Plymouth district. The weekly average figures clearly show that the spawning is intense during the second week of May, which is also true with the surface net records (see Table IV). It may, moreover, be added that the Muller's Top-knot eggs occur principally in April and May in both the nets.

Average Number of Eggs per Haul Week by Week

Week	March	April	May	June
I	0	8.5	13	4 3
II	0	..	14.8	1
III	..	9	9.3	0.7
IV	2	8.5	3 4	0

The size of the eggs and of the oil globule ranges from 0.90 to 1.06 mm. and 0.17 to 0.19 mm. The minimum diameter is usually 0.92 mm., but exceptionally eggs measure 0.91 or 0.90 mm. These dimensions are nearly the same as those given by Hefford (1910) for Plymouth eggs and Ehrenbaum (1905-09) for eggs found in the North Sea. Their monthly average diameter is as under :—

Month	Average Diameter in mm.
April	1.02
May	0.98
June	0.95 (approx.)

SURFACE NET

384 Muller's Top-knot eggs were also recorded from the surface net samples from March 9th to June 1st. The number, both from inside and outside the bay, is not very different and, therefore, it may be stated, for the first time, that Muller's Top-knot eggs are of common occurrence in the area under investigation.

In these hauls the maximum diameter of the egg and oil globule is 1.08 mm. and 0.20 mm. The general size of the egg and oil globule may, thus, be quoted as 0.90 to 1.08 mm. and 0.17 to 0.20 mm. respectively.

17. **Drepanopsetta platessoides** (O. Fabricius)—Long Rough Dab

YOUNG-FISH TRAWL

The Long Rough Dab does not seem to be very common in the Irish Sea and its eggs are only occasionally noted during spring according to the Marine Fauna of the Isle of Man. The fish is probably more common in deep water and that explains the scarcity of eggs near the shore.

It was possible, however, to secure 25 long rough dab eggs from seven drags with the fish trawl in the season under examination. Twenty-three of them occurred in March and April together, none during the following three months and only two in August. Its spawning period in British waters seems to be from February to May or June, but principally in March and April. The occurrence of two eggs in August is thus unusual ; but there is little doubt of the identifications because the egg is characterised by a large pervitelline space and is also large in size. This species, therefore, has probably a longer spawning season than that given in past records.

The egg capsule is very thick and occasionally in a collapsed condition because it is free from the contained yolk. The capsule, besides, appears to have very fine striations and a bluish-green tinge especially under artificial light. These large eggs are 1.37 to 2.04 mm. in size, which is less than that of the North Sea eggs ; but this smaller range is possibly due to the few eggs here examined. Further details about their occurrence are as follows :—

Date	Depth in metres	No.	Diameter in mm.
9-3-39	..	5	1.44—1.68
24-3-39	6.3	1	1.76
18-4-39	5.4	8	1.52—1.90
18-4-39	7.2	8	1.56—2.04
26-4-39	7.2	1	Put in Plunger jar
7-8-39	6.8	1	1.37
14-8 39	5.1	1	1.88

SURFACE NET

This net took only 7 long rough dab eggs, on April 18th, and one of them was found within Port Erin Bay. A comparison of the catches with both the nets shows that the eggs, though meagre in number, occur mainly in April, and that they may be normally found at a little depth below the surface of the water.

18. Pleuronectes limanda (L)—Dab

YOUNG-FISH TRAWL

The dab is common around the Island and its eggs have been recorded in the neighbourhood of Port Erin in the past. 146 dab eggs were taken from twenty-seven young-fish trawl hauls during 1939.

The dab eggs are easily identified because they are small in size amongst the eggs without an oil globule. They contain a clear and colourless yolk which is useful in separating them from smallsized gadoid eggs. Some flounder eggs are likely to resemble them in size, but so far as is known, these are not present off Port Erin.

The eggs occurred on February 10th and ceased after August 14th. The dab like the Rockling and Dragonet has, thus, a prolonged spawning period, which is certainly longer than has been previously recorded for Manx waters. The above eggs, being caught over a period of seven months are not sufficient to fix a main spawning time. The following weekly averages, however, show in general that the eggs occur principally in March and April, and the figures for the surface net catches (see Table IV), excluding the fluctuations early in March, point out in addition that the spawning reaches its maximum in the third week of April. The eggs appear rather irregularly afterwards and finally disappear by the middle of August.

Average Number of Eggs per Haul Week by Week

Week	February	March	April	May	June	July	August
I	0	0	5.5	5	0	1	0
II	2	2	..	4.5	0	2.5	1
III	..	..	15	0	0.2	0	..
IV	5	20	1.5	0.5	0 2	..	0

These eggs are 0.72—0.99 mm. in size which is higher than has been noted from British waters, although nearly the same as from the North Sea. Their approximate monthly diameter is as follows :—

Month	Average Diameter in mm.
February	0.96 (approx.)
March	0.88
April	0.83
May	0.82

SURFACE NET

801 dab egg were found in the surface net as against 146 in the other, although the number of successful hauls was almost the same for both. They are apparently more common near the surface than in the lower layers. It may also be added that the eggs occur in fair number within the bay though these were not as many as outside it.

There occur in the surface net catches some poor cod eggs, the smallest of which approach the largest dab eggs in size. The yolk in the latter, however, is more transparent than in the former and the two may thus be distinguished even when similar in dimensions.

19. **Pleuronectes platessa** (L)—Plaice

YOUNG-FISH TRAWL

The plaice, common in the Irish Sea, commence to spawn early in the year but it was not possible to take regular drags at this time owing to bad weather. Only 88 eggs were therefore obtained from twelve hauls with the young-fish trawl. They were found between February 10th and May 5th but chiefly in March and April (see Tables I and II).

The plaice eggs stand out most prominently because of their large size. The long rough dab eggs are similarly big but they are distinguished from those of plaice by their characteristic perivitelline space. The egg capsule is tough and thicker than in any other of the eggs discussed in this paper. The contained yolk is colourless which usually differentiates them from the larger cod eggs.

These eggs measure 1.61 to 2.04 mm. and the range of size is thus greater than has been noted for British eggs. The maximum diameter of North Sea eggs is 2.20 mm. and it would probably have been higher than 2.04 mm. for our eggs, if hauls had been taken earlier in the season when the maximum number of robust eggs is produced. The following are the average diameters for March and April.

Month	Average Diameter in mm.
March	1.90
April	1.85

SURFACE NET

The surface net samples contained 58 plaice eggs, so that, on the whole, the numbers are small as in the young-fish trawl. A comparison of the catches shows that the eggs are more common outside than inside Port Erin Bay.

20. **Pleuronectes microcephalus** (Donovan) —Lemon Sole

YOUNG-FISH TRAWL

A. Scott (1915) writes that "pelagic eggs identified as those of the lemon sole do not appear to occur very often in the plankton collected at the south-west of the Isle of Man." In 1939, on the contrary, 300 lemon sole eggs were recorded from twenty-six young fish trawl samples. Some of them were successfully reared in plunger jars at the Port Erin Aquarium.

The lemon sole eggs are large but the size is not so marked as in the plaice. In fact they resemble cod eggs in the appearance of the yolk and sometimes in their size, but can be distinguished by their capsule, which bears somewhat irregular markings or reticulations.

The first batch of lemon sole eggs was taken on April 18th and the last on June 21st, but an egg was obtained as late as July 14th with the surface net. The spawning therefore, apparently stretches from April to July, with a maximum in May (see Tables I & II). The weekly figures, besides, illustrate that spawning is intense about the middle of May, a fact also demonstrated by the catches with the surface net (see Table IV).

Average Number of Eggs per Haul Week by Week

Week	April	May	June
I	0	4.6	10.6
II	..	17.1	0
III	2.5	17.6	0.7
IV	0	9.5	0

The diameter of the eggs is 1.14 to 1.48 mm., a range which is similar to eggs obtained from the North Sea. The earlier British records of dimensions are more limited ; probably they were not calculated from material obtained in a systematic manner throughout the spawning season. The average diameter for some months is as given below :

Month	Average Diameter in mm.
April	1.33 (approx.)
May	1.30
June	1.27

SURFACE NET

108 lemon sole eggs appeared in thirteen surface net samples, which shows, in addition, that the eggs of this fish were common around Port Erin during the season under review.

21. Pleuronectes cynoglossus (L)—Witch

YOUNG-FISH TRAWL

Witch eggs, although the adult is found in fair quantities west of Man and off Calf Island, have been recorded on only one occasion, in 1913 by A. Scott (1914) about five miles N. W. by N. from Peel, Isle of Man. They are apparently scarce in this district, which is probably due to the fish resorting to deeper waters for spawning.

It is therefore worthy of note that 36 witch eggs were obtained in the vicinity of Port Erin in 1939. They occurred in eighteen young fish trawl hauls, taken between May 26th and August 1st, and the spawning season is thus slightly later than that of the lemon sole. The presence of eggs in the neighbourhood is further supported by the occurrence of a few witch larvæ towards the end of May and beginning of June. The size of these larval forms, however, suggests that the spawning may have commenced some time before the date given above.

The witch eggs, containing colourless yolk, appear transparent and their egg capsule is thick, although perhaps not as thick as described by Cunningham (1885-87). The capsule, besides, has extremely faint striations, often indistinct or only partly visible.

The diameter is 1.07—1.24 mm., with 1.12 mm. as the mean for may-June, and this range of size is greater than is given in other British records excepting that of Kyle (1903) namely 1.15—1.70 mm. This maximum—1.70 mm.—is unusually high when compared with the measurements in other past records, and is, therefore, open to question.

SURFACE NET

The surface net failed to catch a single witch egg, which further points to its general dearth in the area under investigation.

22. **Solea vulgaris** (Wuensel)—Sole

YOUNG-FISH TRAWL

The sole is frequently taken around the Island but its eggs were not recorded from South-west of the Isle of Man even during 1907-12, the period of intensive plankton investigations. A. Scott (1914) has noted some eggs from an area, many miles off Port Erin, but during the present investigations in 1939, 46 sole eggs were procured near to Port Erin at the different depths fished by the young-fish trawl.

There is no doubt about their identification because some of them were hatched out and reared in the Biological Station, Port Erin. In addition the curious oil globules, which are arranged into several irregular aggregates over the yolk, are the surest means of identifying these eggs.

The eggs, 42 of which were found in the month of May alone, appeared between April 28th and June 1st. The spawning seems to commence in April in this area, although even earlier in the Plymouth district. The size of the few eggs measured is 1.23 to 1.44 mm. which is very near to other previous records.

SURFACE NET

The surface net recorded only a single sole egg on May 18th, a further proof of their general scarcity in the neighbourhood of Port Erin.

23. **Solea variegata** (Fleming)—Variegated Sole

YOUNG-FISH TRAWL

Hardman (1902) states that "it occurs in our district, and is caught occasionally in the trawl in various parts of the Irish Sea." There is, however, no record of *S. variegata* or its eggs in the Marine Fauna of the Isle of Man, and it is therefore interesting to report here on nine eggs of this fish, collected during the season under review.

These eggs are characterised by many rather large oil globules, scattered separately over the surface of the yolk and not in groups like in *S. vulgaris*. The oil globules are usually similar in size but not necessarily so in every case. The thick egg capsule has markings somewhat resembling those in lemon sole eggs ; this is a feature that seems to have escaped the attention of other workers.

Cunningham (1889-90) has recorded *S. variegata* eggs in July, and Hefford (1910) in April, May, June and August at Plymouth where they occur in large numbers. Eight out of the nine eggs noted here were found in June and one in August. The spawning period may, thus, be provisionally accepted as from April to August.

Further particulars of these eggs are as follows :

Date	Depth in metres	No.	Diameter in mm.
21-6-39	5.4	6	1.29—1.42
21-6-39	6.3	2	1.38—1.42
7-8-39	6.8	1	1.28

The presence of young embryos within these eggs shows that they had been spawned sometime previous to the date of capture and they were probably carried into this area from some outside spawning ground.

24. **Solea lutea** (Bonaparte)—Solenette

SURFACE NET

The eggs of *S. lutea* are noted in the Marine Fauna of the Isle of Man as taken occasionally in the spring and early summer. Six solenette eggs were also found in three surface net samples from Port Erin Bay in March and April 1939.

These small eggs are characterised by many small and almost equal sized oil globules, distributed over the surface of the yolk. A. Scott (1913) writes that the oil globule in the egg of the rockling sometimes splits up into a number of smaller ones and further states that the eggs he had identified as those of solenette were possibly the newly spawned eggs of rockling. This, however, seems to be highly improbable because the smaller globules formed by the splitting up of the rockling oil globule are neither so numerous nor so regularly arranged as in the solenette. In addition the total size of the numerous oil globules in the solenette is certainly bigger than that of the single oil globule in the rockling egg. The diameter of these eggs is 0.70 to 0.77 mm.

SUMMARY

1. 24,735 fish eggs, assigned to twenty-four species, have been dealt with in this report. 10,879 of them were obtained with a young-fish trawl and 13,856 with a surface tow-net.

2. The area under review, especially the part near the Calf Sound, is prolific in the number and variety of fish eggs and larvae. Certain hauls from the Port Erin Bay, however, show sudden fluctuations in the catch which is presumably due to weather conditions, inshore winds in particular.

3. The first batch of eggs occurred on February 10th and the last on October 12th. They were abundant in March, April and May, rare in September and October and there were none in November and December.

4. Eggs of Sprat, Cod, Whiting, Five-Bearded Rockling, Dragonet, Muller's Top-knot, Grey Gurnard, Dab, and Lemon Sole are common in this connection.

5. The eggs, particularly of *A. sphyraena*, *O. cimbrius*, *C. julis*, and *S. variegata* are new additions to the Manx Fauna.

6. The occurrence of eggs of *R. maximus*, *S. norwegicus*, *P. cynoglossus* and *S. vulgaris* in large numbers is a definite contribution to their past occasional records from this area.

7. Sprat eggs were more abundant in this water than hitherto expected. The graph of the spawning of sprat shows, as in some other species, that the peak of spawning is very marked showing that its maximum spawning extends over a few days.

8. The occurrence of Ling eggs and larvae is new evidence that the fish spawns to the west of the Island in deeper waters.

9. The maximum diameter of *C. rupestris* eggs is higher than that recorded in literature.

10. Judging from the present observations there is an indication of a spawning period longer than previously noted in these waters for some species, e.g. Ling, Long Rough Dab, etc.

11. It may be generally stated that in this collection the average size of fish eggs diminished with the advance of spawning season.

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TABLE I

Monthly Summary of the Occurrence of Pelagic Fish Eggs in the Young-Fish Trawl, Port Erin, 1939.

Month	Jan.	Feb.	Mar.	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Total No. of Eggs per species
No. of Hauls	0	3	3	6	23	13	7	13	9	4	9	5	
C. sprattus	..	..	..	212	1568	304	147	26	..	..	..	..	2257
A. sphyræna	..	..	..	1	7	..	..	..	..	..	..	..	8
G. callarias	..	19	234	813	239	..	..	..	..	..	..	..	1305
G. minutus	..	..	..	..	..	..	..	..	..	..	..	..	0
G. merlangus	..	81	326	3288	1113	6	..	..	..	..	..	..	4814
M. molva	..	..	..	3	15	23	65	70	..	..	..	..	176
O. mustela	..	..	67	81	176	42	6	6	2	..	..	..	380
O. cimbrius	..	..	..	..	..	21	14	13	2	..	..	..	50
C. julis	..	..	..	..	..	..	..	5	..	..	..	..	5
C. rupestris	..	..	..	..	..	..	..	43	2	1	..	..	46
C. lyra	..	1	18	114	290	25	..	..	..	..	..	..	448
C. maculatus	..	..	..	..	..	2	..	..	..	..	..	..	2
T gurnardus	..	..	1	40	229	79	19	11	..	..	..	..	379
R. maximus	..	..	..	..	6	14	16	7	1	..	..	..	44
S. norwegicus	..	..	..	..	6	11	3	3	..	..	..	..	23
Z. punctatus	..	..	2	52	221	17	..	..	..	..	..	..	292
D. platessoides	..	..	6	17	..	..	..	2	..	..	..	..	25
P. limanda	..	7	22	44	61	2	7	3	..	..	..	..	146
P. platessa	..	5	26	54	3	..	..	..	..	..	..	..	88
P. microcephalus	..	..	..	5	260	35	..	..	..	..	..	..	300
P. cynoglossus	..	..	..	..	18	7	6	5	..	..	..	..	36
S. vulgaris	..	..	..	1	42	3	..	..	..	..	..	..	46
S. variegata	..	..	..	..	..	8	..	1	..	..	..	..	9
S. lutea	..	..	..	..	..	..	..	..	..	..	..	..	0
Total Number of Eggs per Month ..	0	113	702	4725	4254	599	283	195	7	1	..	..	10879

TABLE II

Monthly Summary of the Occurrence of Pelagic Fish Eggs in the Surface Net, Port Erin, 1939.

Month	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Total No. of Eggs per Species
No. of Hauls	0	1	8	11	10	6	4	5	4	2	3	2	
C. sprattus	..	..	4	603	287	69	33	2	..	..	..	..	998
A. sphyræna	..	..	..	..	..	..	..	..	..	..	..	..	0
G. callarias	..	..	528	873	14	..	..	..	..	..	..	..	1415
G. minutus	..	..	173	126	..	..	..	..	..	..	..	..	299
G. merlangus	..	1	1148	1780	143	..	..	..	..	..	..	..	3072
M. molva	..	..	..	4	..	..	5	3	..	..	..	..	12
O. mustela	..	..	3864	1557	306	50	17	24	..	..	..	..	5818
O. cimbrius	..	..	..	..	..	8	1	2	..	..	..	..	11
C. julis	..	..	..	..	1	1	1	..	..	..	..	..	3
C. rupestris	..	..	..	..	..	..	..	10	..	..	..	..	10
C. lyra	..	..	193	395	193	22	4	..	..	..	..	..	807
C. maculatus	..	..	..	..	2	1	1	1	..	..	..	..	5
T. gurnardus	..	..	..	16	17	6	..	..	..	..	..	..	39
R. maximus	..	..	..	..	..	..	..	1	..	..	..	..	1
S. norwegicus	..	..	..	1	..	..	..	..	..	..	..	..	1
Z. punctatus	..	..	16	223	144	1	..	..	..	..	..	..	384
D. platessoides	..	..	..	7	..	..	..	..	..	..	..	..	7
P. limanda	..	..	363	398	29	1	10	..	..	..	..	..	801
P. platessa	..	..	31	26	1	..	..	..	..	..	..	..	58
P. microcephalus	..	..	..	..	102	5	1	..	..	..	..	..	108
P. cynoglossus	..	..	..	..	..	..	..	..	..	..	..	..	0
S. vulgaris	..	..	..	..	1	..	..	..	..	..	..	..	1
S. variegata	..	..	..	..	..	..	..	..	..	..	..	..	0
S. lutea	..	..	5	1	..	..	..	..	..	..	..	..	6
Total Number of Eggs per Month ..	0	1	6325	6010	1240	164	73	43	0	0	0	0	13856

TABLE III

Weekly Averages of Pelagic Fish Eggs per Haul with the Young-Fish Trawl, Port Erin, 1939.

Month	Feb.				March				April				May				June				July				August				Sept.				Oct.			
Week	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV
No. of Hauls per Week	1	1	0	1	1	1	0	1	2	0	2	2	6	6	3	8	3	1	4	5	2	2	3	0	5	3	0	5	2	0	2	5	0	2	2	0
C. sprattus	..	..	..	..	..	..	..	..	11.5	..	63.5	31	25.1	48.3	219.3	58.6	38.6	2	25.7	16.6	16.5	31	17.3	..	5.2	..	..	..	..	..	..	..	..	..	..	..
A. sphyræna	..	..	..	..	..	..	..	..	0.5	..	..	..	0.2	0.7	0.3	0.1	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
G. callarias	..	1	..	18	6	14	..	214	59.5	..	314	6	23.8	15.3	1.3	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
G. minutus	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
G. merlangus	..	15	..	66	21	63	..	242	837	..	752	55	80.8	90.1	7.6	8	2	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
M. molva	..	..	..	..	..	..	..	..	..	..	1	0.5	0.6	0.5	0.6	0.7	..	..	5.2	0.4	11	1.5	13.3	..	12.4	2	..	0.4	..	..	..	..	..	..	..	..
O. mustela	..	..	..	..	37	2	..	28	9.5	..	23.5	7.5	5	10.6	4	8.7	8.6	1	3.5	0.2	0.5	2	0.3	..	1.2	..	..	..	0.5	..	..	0.2	..	..	..	..
O. cimbrius	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	4.5	0.5	1.5	4.5	0.7	..	2	0.3	..	0.4	..	..	..	0.4	..	..	..	..
C. julis	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	0.8	..	..	0.2	..	..	..	..	..	..	..	..
C. repestris	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	5.6	3	..	1.2	1	..	..	..	..	0.5	..	..
C. lyra	..	..	..	1	6	2	..	10	13.5	..	41.5	2	18.3	18	7.3	6.2	5	..	2.5	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
C. maculatus	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	0.5	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
T. gurnardus	..	..	..	..	..	..	..	1	1	..	14	5	4.1	17.3	3.7	11.1	8.3	1	12.5	0.6	1.5	4	2.6	..	2	0.3	..	..	..	..	..	..	..	..	..	..
R. maximus	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	0.7	0.7	..	2.2	0.6	2	2.5	2.3	..	1	0.7	..	..	0.5	..	..	..	..	..	..	..
S. norwegicus	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	0.7	2	..	1	0.2	1	..	0.3	..	..	..	..	0.6	..	..	..	..	..	..	..	..
Z. punctatus	..	..	..	..	..	..	..	2	8.5	..	9	8.5	13	14.8	9.3	3.4	4.3	1	0.7	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
D. platessoides	..	..	..	..	..	5	..	1	..	..	8	0.5	..	..	..	..	..	..	..	..	..	..	..	..	0.2	0.3	..	..	..	..	..	..	..	..	..	..
P. limanda	..	2	..	5	..	2	..	20	5.5	..	15	1.5	5	1.5	..	0.5	..	..	0.2	0.2	1	2.5	..	..	..	1	..	..	..	..	..	..	..	..	..	..
P. platessa	..	3	..	2	1	11	..	14	9.5	..	14	3.5	0.5	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
P. microcephalus	..	..	..	..	..	..	..	..	..	..	2.5	..	4.6	17.1	17.6	9.5	10.6	..	0.7	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
P. cynoglossus	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	2.2	0.3	..	1.2	0.2	0.5	1	1	..	1	..	..	..	..	..	..	..	..	..	..	..
S. vulgaris	..	..	..	..	..	..	..	..	..	..	..	0.5	2.1	1.6	3.7	1	1	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
S. variegata	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	2	..	..	..	..	..	0.2	..	..	..	..	..	..	..	..	..	..	..
S. lutea	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..

TABLE IV

Weekly Averages of Pelagic Fish Eggs per Haul with the Surface Net, Port Erin, 1939.

Month	FEB	MARCH				APRIL				MAY				JUNE				JULY				AUGUST			
Week	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV
No. of Hauls per Week	1	0	2	2	4	3	0	4	4	4	2	1	3	1	0	4	1	2	1	1	0	2	1	0	2
C. sprattus	0	..	0	0	1	0	..	131	19.75	23.75	52	50	12.66	11	..	14.25	1	6	14	7	..	1	0	..	0
A. sphyræna	0	..	0	0	0	0	..	0	0	0	0	0	0	0	..	0	0	0	0	0	..	0	0	..	0
C. callarias	0	..	155	29	40	17.33	..	202.5	2.75	3.5	0	0	0	0	..	0	0	0	0	0	..	0	3	..	0
G. minutus	0	..	47	17.5	11	30	..	9	0	0	0	0	0	0	..	0	0	0	0	0	..	0	0	..	0
G. merlangus	1	..	407.5	89	38.75	220.66	..	252.5	27	21.25	25.5	1	2	0	..	0	0	0	0	0	..	0	0	..	0
M. molva	0	..	0	0	0	0	..	0.5	0.5	0	0	0	0	0	..	0	0	1	1	2	..	1.5	0	..	0
O. mustela	0	..	472	933.5	263.25	78.66	..	255.75	74.5	29.25	70	10	13	9	..	10	1	5	4	3	..	11.5	0	..	0.5
O. cimbrius	0	..	0	0	0	0	..	0	0	0	0	0	0	0	..	2	0	0	1	0	..	0	0	..	1
C. julis	0	..	0	0	0	0	..	0	0	0.25	0	0	0	0	..	0.25	0	0.5	0	0	..	0	0	..	0
C. rupestris	0	..	0	0	0	0	..	0	0	0	0	0	0	0	..	0	9	0	0	0	..	1	6	..	1
C. lyra	0	..	48.5	14.5	16.75	13.66	..	68.75	19.75	17.75	50	7	5	6	..	3.75	1	1	2	0	..	0	0	..	0
C. maculatus	0	..	0	0	0	0	..	0	0	0	0.5	0	0.33	0	..	0	1	0	0	1	..	0.5	0	..	0
T. gurnardus	0	..	0	0	0	0	..	3.75	0.25	0.5	4	0	2.33	3	..	0.75	0	0	0	0	..	0	0	..	0
R. maximus	0	..	0	0	0	0	..	0	0	0	0	0	0	0	..	0	0	0	0	0	..	0.5	0	..	0
S. norwegicus	0	..	0	0	0	0	..	0	0.25	0	0	0	0	0	..	0	0	0	0	0	..	0	0	..	0
Z. punctatus	0	..	1	5.5	0.75	6.66	..	40.5	10.25	6.5	57	1	1	1	..	0	0	0	0	0	..	0	0	..	0
D. platessoides	3	..	0	0	0	0	..	1.75	0	0	0	0	0	0	..	0	0	0	0	0	..	0	0	..	0
P. limanda	0	..	125.5	13	21.5	18.66	..	81.75	3.75	4	6.5	0	0	0	..	0	1	0	8	2	..	0	0	..	0
P. platessa	0	..	13.5	0	1	1.66	..	5	0.25	0.25	0	0	0	0	..	0	0	0	0	0	..	0	0	..	0
P. microcephalus	0	..	0	0	0	0	..	0	0	7.25	29	5	3.33	3	..	0.5	0	0	1	0	..	0	0	..	0
P. cynoglossus	0	..	0	0	0	0	..	0	0	0	0	0	0	0	..	0	0	0	0	0	..	0	0	..	0
S. vulgaris	0	..	0	0	0	0	..	0	0	0	0	1	0	0	..	0	0	0	0	0	..	0	0	..	0
S. variegata	0	..	0	0	0	0	..	0	0	0	0	0	0	0	..	0	0	0	0	0	..	0	0	..	0
S. lutea	0	..	1.5	1	0	0.33	..	0	0	0	0	0	0	3	..	0	0	0	0	0	..	0	0	..	0

DIGESTIVE GLANDS OF THE SCORPION

A Physiological Investigation

By

JER K. BARDI, AND C. J. GEORGE

Department of Biology, Wilson College, Bombay

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INTRODUCTION AND HISTORICAL SURVEY

SITUATED in the Meso-soma of the Scorpion is a much lobulated glandular organ, the liver (Fig. 1). It fills up most of the body-cavity of that region on either side of the mid-gut. The lobularity of this organ is chiefly due to the shape of the body-cavity, and differs in the various species of scorpions. Five pairs of ducts issue out of the liver and open into the mid-gut. The presence of five pairs of ducts shows that in the development of this organ, five glands have fused together on either side.

This glandular lobulated organ has been known since the days of the early anatomists.

Gueysse in 1808-1809, Meckel in 1809, Blanchard in 1854 and Dufour in 1855 called it—the "liver." Whereas Treviranus in 1912 called it the "fat-body." Newport (1843)—on the other hand—believed that it was a "blind glandular appendage of the mid-gut."

Just in front of the liver, placed in the pro-soma or cephalothorax, is a five-lobed glandular body, consisting of a median un-paired lobe and two pairs of lateral ones. But this organ is totally unconnected with the liver being separated from the latter by the endosternite, which divides the pro-soma from the meso-soma. This organ, in its colour, the character of tissue and consistency, appears exactly similar to the liver, so much so, that, at first sight, it is difficult to distinguish it from the latter. It opens by means of a pair of ducts into the anterior portion of the mid-gut, the stomach.

This gland has been called by various names by various investigators. T. Muller in 1828, and Newport in 1843, called it the "Salivary gland"—(so encountered also in several Text-books of Zoology). Dufour, in 1856, took it as the "cephalothoracic outgrowth of the liver" and regarded the coxal glands as the true salivary glands. E. Blanchard, in 1858-59, showed that the scorpions were devoid of salivary glands, and that the organ looked upon as salivary gland by Muller and Newport, was nothing else but "stomach glands."

The question whether the two digestive glands—the "liver" and the so-called "stomach glands"—of the scorpion are really two different organs or whether they are analogous, has been under discussion for a long time. In 1926, Pavlovsky and Zarin studied the physiological aspect of this question in detail. They determined the ferments in the two organs and arrived at the conclusion, that the liver differed definitely from the stomach glands in its ferment contents though not histologically, and that they were not analogous organs and therefore deserved distinct names. But from a perusal of their paper it is gathered that their investigations were far from complete.

In order to throw further light on this controversial subject, the present physiological work was undertaken on these two digestive glands of *Palamnaeus fulvipes* Koch.

Some previous authors had also worked on similar lines, on the ferments of scorpions. Blanchard, in 1851, tested the proteolytic ferments of the stomach glands of scorpions. Later, in 1855, he studied the functions of the liver in other Arachnids besides that of the scorpion.

Krukenberg in 1881, Fischer in 1903 and Kobert in 1913, worked on the different enzymes in scorpions. They made use of preserved alcoholic specimens of scorpions in preparing the extracts. Since the method employed in the extraction of the ferments was not satisfactory, the presence of the ferments was not readily detected by them. In spite of this, they were able to establish the presence of the ferment Amylase in the scorpion. Kobert, in 1913, discovered the presence of Inulase, and Krukenberg and Fischer obtained also the ferment Trypsin.

All the same, the work carried out by the various authors has not been exhaustive, except that of Pavlovsky and Zarin. But since these two authors also were handicapped by lack of sufficient material, their entire work being done on the material obtained from only seven scorpions, the results obtained by them cannot be taken as conclusive. This state of affairs has prompted us to work out this problem. We were able to obtain specimens of Palamnaeus in large numbers at all times of the year —and so we were able to experiment on fresh materials obtained from dozens of scorpions at a time. Hence, we had ample scope for repeating our experiments and verifying the results so as to obtain conclusive evidence.

MATERIAL AND METHOD

Glycerine extracts of the digestive organs (liver, stomach glands and mid-gut) of the scorpion Palamnaeus were separately prepared in the following manner :

The scorpions were dissected in normal saline solution immediately after chloroforming them.

The liver, the stomach glands and the mid-gut were separated from the surrounding tissues and the adhering fluid was removed with blotting paper.

Approximately equal quantities of the liver and the stomach glands were taken and ground separately in porcelain mortars along with pure, roasted, acid-free sand and equal quantities of pure glycerine, till the tissues became very fine and completely mixed with the glycerine. (The sand was used to facilitate the crushing of the tissues into a fine mash). The two extracts (of about equal concentration) were then emptied into separate glass stoppered bottles and to each a few drops of toluol were added as a preservative.

The extract of the mid-gut was similarly prepared, but as the size of this organ is very small, its extract could not be kept at the same concentration as those of the other two organs.

The liver is a very massive organ in comparison with the stomach glands, and therefore only a small portion of it, about as much as the whole of the stomach glands, could be utilized in the preparation of its extract in order to keep the concentration of the two extracts equal. The rest of the liver however was not wasted. We prepared more concentrated liver extract, and made use of this whenever we wanted to amplify the results of the weaker solutions.

Though these extracts remain in good condition at room temperature for several months, only a small quantity was prepared at a time as live scorpions were readily available whenever required.

Each time a dozen scorpions were dissected and, as already mentioned, care was taken to keep the concentration of the extract of liver and stomach glands equal as far as possible.

THE ENZYMES OF THE DIGESTIVE ORGANS OF SCORPION

The extracts were tested for the following enzymes :—Chymosin, Pepsin, Trypsin, Invertase, Lipase, Inulase, Amylase and Catalase.

1. Chymosin

Milk is coagulated by Chymosin or rennet ferment. The action of the ferment is such, that, in the presence of a sufficient quantity of calcium salts, the greater part of casein which is contained in the milk is precipitated in the form of paracasein.

There is no literature regarding the presence of Chymosin in the digestive glands of the scorpion, except that of Pavlovsky and Zarin.

PROCESS

For the detection of Chymosin 10 c.cs. of milk were taken and mixed with 90 c.cs. of distilled water. To this, 1 c.c. of 10% calcium chloride was added. 5 c.cs. each of this mixture were taken in four test tubes, in the first three of which 2 c.c.s of the glycerine extracts of liver, stomach glands, and mid-gut respectively were added. In the fourth test tube 2 c.cs. of pure glycerine only were added as a control. All the tubes were kept in a water bath at 40° c. for 10 to 20 minutes.

RESULTS

Control Solution :—In the test tube containing the control solution no coagulation of the casein of the milk was observed.

Liver and Stomach glands Extracts :—In the two test tubes containing respectively the extracts of the liver and the stomach glands the casein of the milk coagulated after 10 minutes and the amount of precipitate in both the tubes appeared almost equal.

The experiment was repeated five times and the result obtained each time was positive, proving the presence of Chymosin in the extracts.

Mid-gut Extract :—The test tube containing the extract of the midgut did not show any coagulation of the milk for over twenty minutes, and so it was left for several hours in the water bath, together with the test tube containing the control solution. When examined after four hours, a foamy curd-like precipitate was found in the mid-gut solution. The control solution also had a foamy appearance but there was no curd-like precipitate in it. This experiment was repeated only twice, as the quantity of the mid-gut extract was limited, and similar results were obtained in both the experiments.

The above series of experiments were duplicated without the addition of calcium chloride to the solutions. The result in each case was negative. There was no precipitate formed in the solution. This shows that the presence of a calcium salt is necessary for the enzyme to act on the casein.

According to Pavlovsky and Zarin, in the solution containing the extract of the stomach glands, the casein of the milk coagulated after

50 minutes, and that too only once in three experiments, while in the solution containing the extract of the liver, casein coagulated in 10 minutes in all the three experiments conducted by them. This difference may be rather due to the unequal concentrations of the two extracts. We have not found any difference in the time taken for coagulation, between the two extracts, in any of our experiments.

In order to ascertain whether concentration of the extracts had anything to do with the difference in the time taken for coagulating, we made several tests with the liver extracts of two different concentrations and in all these tests the coagulation of the casein took place more rapidly in the more concentrated extracts than in the less concentrated one.

2. Pepsin

The presence of Pepsin in liver and stomach glands of the scorpion was ascertained by means of the gelatin test.

PROCESS

30 gms. of powdered gelatin were shaken up with 100 c.cs. of distilled water in an evaporating dish. The gelatin solution was not heated directly but was kept in a water bath, till the solution was rendered clear and homogeneous. Next, it was made acidic by the addition of a few drops of concentrated hydrochloric acid, though gelatin itself in solution was found to be slightly acidic.

The acidulated gelatin solution was poured into four flat-bottomed glass tubes, about 3 c.c.s. in each, and then kept in ice for setting. After the gelatin was set, 2 c.c.s of the extracts of liver, stomach glands and mid-gut were added to the gelatin in the first three tubes respectively, and to the gelatin in the fourth tube 2 c.cs. of pure glycerine only were added as a control. The level of the gelatin in each tube was marked by sticking a slip of paper outside the tube. The tubes were corked and left at room temperature for one day.

RESULTS

Control :—There was no liquefaction of the gelatin.

Liver and Stomach glands Extracts :—In the tubes containing the extracts of liver and stomach glands, a portion of the gelatin was found liquefied at the top. The quantity of the liquefied gelatin was about the same in both the tubes.

Mid-gut Extract :—The gelatin was not liquefied.

7 experiments were carried out with 30% gelatin and the results obtained each time were the same. The process of liquefaction of the gelatin by the ferment Pepsin of the digestive glands started within a few minutes of the setting up of the experiments.

In 6 other experiments, where 10% to 25% gelatin was used, the gelatin did not set even in ice. These experiments had therefore to be abandoned.

Pavlovsky and Zarin used only a 10% solution of gelatin and got satisfactory results. And in their experiments the process of liquefaction of the gelatin did not commence until after two days.

3. Trypsin

The presence of the tryptic ferments in the scorpion was mentioned by Krukenberg and Fischer, and also by Pavlovsky and Zarin.

To ascertain the presence of Trypsin in the digestive glands of the scorpion we made the following two tests :—

A. Gelatin test, and

B. Casein test.

A. THE GELATIN TEST

PROCESS

In this test, both neutral and alkalized gelatin of the same concentrations were used..

30 gms. of powdered gelatin were taken and dissolved in 100 c. cs. of distilled water, in an evaporating dish, and placed in a water bath, till the gelatin solution was clear and homogeneous. The gelatin solution as such is little acidic, so in order to make it neutral about 3 c. cs. of dilute KOH (about 10 to 15 %) was added to 50 c.cs. of the gelatin solution and to the other 50 c.cs. of the gelatin solution, about 5 c. cs. of the same dilute KOH were added to make the solution alkaline.

The neutral solution of gelatin was poured into 4 small, flat-bottomed, glass tubes, and the alkalized solution was likewise poured into another set of 4 similar tubes. The level of the gelatin in each tube was marked by pasting a slip of paper outside. The 8 tubes were labelled as follows :

1) Neutral Liver,
2) Neutral St. glands,
3) Neutral Mid-gut,
4) Neutral Control,
5) Alkalized Liver,
6) Alkalized St. glands,
7) Alkalized Mid-gut,
8) Alkalized Control.

All the tubes were kept in ice to set the gelatin. Then 2 c.cs. of the glycerine extracts of liver, stomach glands and mid-gut were poured into the respective tubes. In the control tubes pure glycerine was poured. These eight tubes were allowed to remain at room temperature (about 30°c.) for 24 hours.

RESULTS

Control Solution (*neutral gelatin*) :—The gelatin in this remained unaltered after 24 hours.

Liver and Stomach glands Extracts (*neutral gelatin*) :—In the tubes containing the extracts of the liver and the stomach glands the gelatin had undergone liquefaction at the top. In both the tubes equal quantities of the gelatin had liquefied but in two experiments the liquefaction had proceeded more in the extract of the stomach glands than in the extract of the liver.

Mid-gut (neutral gelatin) :—The gelatin in this remained unaltered.

Control (alkalized gelatin) :—The gelatin here remained unaltered.

Liver and Stomach glands (alkalized gelatin) :—In both the tubes liquefaction of the gelatin had taken place as in the case of the extracts with neutral gelatin. In some experiments the amount of gelatin liquefied was almost the same as in the case with the neutral gelatin but in others it was slightly greater. The quantity of gelatin liquefied in the two tubes was equal.

Mid-gut (alkalized gelatin) :—The gelatin here remained unchanged.

B. THE CASEIN TEST

Casein is precipitated by acetic acid, but in the presence of Trypsin, Casein is split up and the resulting substances do not precipitate on the addition of acetic acid. Casein is dissolved by heating in a small quantity of water in the presence of a 10% solution of Soda (NaOH). This method was introduced by Grass, Fuld and Michaelis (Aberhalden, 1910).

PROCESS

For our experiments 0.2 gm. of Casein was taken in an evaporating dish to which a spoonful of distilled water and about 3 c.c.s. of 10% NaOH were added. The solution was boiled for about 5 minutes till all the casein was dissolved. To this, distilled water was added till the solution amounted to 100 c.cs. The solution was then filtered and from the clear filtrate 5 c.cs. each were taken in three test tubes. To one of these 2 c.cs. of the liver extract and to the second 2 c.c.s. of the stomach glands extract were added. To the third 2 c.c.s of pure glycerine and a few drops of toluol were added as control. The test tubes were then immersed in a water bath at 40°c. After one hour the solutions were allowed to cool and again filtered as they were not sufficiently transparent.

At a time only half of the contents of each tube was tested with 0.25% acid, added carefully by drops and the changes noted.

RESULTS

Control :—In the control solution a white chalky precipitate was at once obtained on the addition of a single drop of the acetic acid.

Liver and Stomach glands :—In the solutions containing the extracts of the liver and the stomach glands a very slight white precipitate was visible but that on the addition of many drops of the acetic acid. The precipitates in the two tubes were almost equal.

These experiments were conducted four times with the same results.

In one experiment one set of solutions were kept in the water bath as usual, while another set of similar solutions was tested immediately on preparation and so not allowing the ferment time enough to act on the casein. The results of the two sets were compared. The precipitates obtained in the latter case were definitely greater than in the solutions kept in the water bath for an hour, showing that the ferment had not acted on the casein.

The results would indicate that the ferment Trypsin is present in both the liver and the stomach glands of the scorpion and in equal strength.

Pavlovsky and Zarin in their experiments on Trypsin with the Gelatin Test obtained positive results for both the liver and the stomach glands, although they mention that gelatin did not liquefy so energetically with the stomach glands extract as with the liver extract.

In their experiments with the Casein Test, however, they obtained positive results in all their three experiments with the liver extract and negative results in all the three experiments with the stomach glands extracts. That was due, according to them, to the fact that gelatin presents a more sensitive reagent to Trypsin than does Casein.

But the fact that they did not get a positive result in the case of the stomach glands may be due, we think, to the difference in the concentrations of their extracts as may be judged also from the results of their Gelatin Test.

4. Invertase

With the help of the ferment Invertase, cane-sugar absorbs water and is split up into grape sugar and fruit sugar.

Invertase is not known in the scorpion, though it is widespread in the animal and vegetable kingdoms along with a number of other enzymes.

METHOD

For the detection of Invertase 5 gms. of cane-sugar were dissolved in 100 c.cs. of distilled water. Like this, three solutions were prepared and kept in bottles. In the first two, 5 c.cs. of the glycerine extracts of liver and stomach glands were added respectively. While in the third, 5 c.cs. of pure glycerine only were added as a control. In all three, a few drops of toluol was added as preservative. The mixtures thus prepared, were allowed to remain in the thermostat for 2 days at 30°c. At the end of this period the solutions were taken out, and examined. The solutions containing the extracts of liver and stomach glands were too opaque to transmit light, when put into the polarimeter. So they were filtered through double filter paper till they became somewhat transparent.

RESULTS

One after another the solutions were put in the polarimeter. Readings were taken at intervals of 2 hours each but no change was observed in the rotation in all the three solutions. The solutions were allowed to remain in the polarimeter for more than 24 hours. Still there was no change. This shows that the cane sugar was not split up and that therefore the ferment Invertase is absent. The experiments with all the three solutions were repeated, with the same results.

5. Lipase

The methods of estimating the fat-splitting ferments or Lipases are based on the capability of these ferments to split fats into free fatty acids and glycerine.

There is no data in the literature regarding the fat-splitting ferments in the digestive glands of the scorpion, except the work of Pavlovsky and Zarin.

METHOD

In order to estimate the ferment Lipase in the digestive glands of the scorpion the following process was followed :

10 c.cs. of olive oil were taken in a glass bottle, and to it distilled water was added till the solution amounted to 100 c.cs. The solution was then thoroughly shaken till the olive oil was completely mixed with the water and did not separate out.

From the olive oil emulsion 10 c.cs. each were taken in 4 different test tubes, to three of which were added 2 c.cs. of the glycerine extracts of liver, stomach glands and mid-gut respectively. To the fourth tube 2 c.cs. of pure glycerine only were added as control. All the tubes were put in the water bath at 37°c. for 24 hours, and then at 55 °c. for 2 hours. After this the solutions were allowed to cool.

In the meantime a quantity of 50% solution of ether alcohol ($\frac{1}{2}$ ether + $\frac{1}{2}$ absolute alcohol) and a $\frac{N}{10}$ solution of NaOH were prepared.

When the tubes were completely cooled, 5 c.cs. of the solution from each tube were taken in a small beaker one after another and to these 10 c.cs. of the ether-alcohol mixture and one drop of phenolphthalein were added. The mixture was then titrated against the $\frac{N}{10}$ solution of NaOH. The quantity of NaOH used up in the titration was noted.

RESULTS

Control :—The control solution turned permanently pink in colour on the addition of only a single drop of the NaOH solution.

Liver and Stomach glands :—In the solutions containing the extracts of the liver and the stomach glands, several drops of NaOH solution were required to change the colour to permanent pink, thus indicating that these solutions were more acidic than the control solution. The burette readings for both the extracts were almost equal.

Mid-gut :—The solution containing the extract of the mid-gut gave a permanent pink colour with only one drop of NaOH as in the case with the control solution.

Two readings were taken in each experiment and the mean calculated. In order to get the figures for the increase of acidity in the solutions tested as compared with the control, the burette reading for the control solution was subtracted from those for the liver, the stomach glands, and the mid-gut extracts. The increase of acidity in the liver and the stomach glands solutions was almost equal.

Increase in the acidity of the solutions shows that the olive oil was split up forming fatty acids.

The results would indicate therefore that the ferment Lipase is present in the liver and the stomach glands in almost equal concentration, while it is absent in the mid-gut.

According to Pavlovsky and Zarin, the stomach glands extract showed an increase of acidity equivalent to .1 c.c. of $\frac{N}{10}$ NaOH only in one of the three experiments they performed, while the liver extract showed an increase of acidity equivalent to .16 c.c. of $\frac{N}{10}$ NaOH in the first, .55 c.c. in the second, and .2 c.c. in the third experiment.

We have found an increase in the acidity of the stomach glands extract in all our experiments and that too about as much as the increase in the acidity of the liver extract.

The difference in the figures of the increase of acidity in the liver extracts given by Pavlovsky and Zarin may be due to the difference in the concentrations of the liver extracts they used for their three experiments. Because, in one of our experiments we used the more concentrated liver extract and consequently the readings showed an increase of acidity equivalent to .6 c.c. of $\frac{N}{10}$ NaOH as compared with .2 c.c. of $\frac{N}{}$ NaOH of the weaker extract.

6. Inulase

In some plants, especially the Compositæ, besides starch and glycogen, there is a carbohydrate inulin.

Under the influence of a special ferment Inulase, inulin is converted into fructose.

Kobert discovered Inulase in scorpions. According to him, a solution of inulin to which the extract of scorpions preserved in alcohol was added, reduced Fehling's liquid after 48 hours. Pavlovsky and Zarin have contradicted Kobert as regards this enzyme.

METHOD

For testing the ferment Inulase, 1 gm. of inulin was dissolved in 100 c.cs. of distilled water, after continuous shaking. From this 1% solution of inulin, 10 c.cs. each were taken in 3 test tubes and to the first two were added 3 c.cs. of the glycerine extracts of liver and stomach glands respectively and 5 drops of toluol as a preservative. The third tube was prepared as a control solution with 3 c.cs. of pure glycerine only instead of the extract. The three test tubes were put into the thermostat at 40°c. and were allowed to remain there for about 48 hours. After this period, the test tubes were taken out and the contents cooled. From the contents of the test tubes little quantities of the solutions were taken into smaller test tubes, and a few drops of Fehling's Solution were added. On the addition of Fehling's Solution, a blue colour was obtained in all the three test tubes. The mixtures were then heated on a Bunsen burner and colour changes (if any) were noted.

RESULTS

Control:—The control solution remained unchanged showing the same clear blue colour.

Liver and Stomach glands :—The solutions containing the extract of the liver and the stomach glands of the scorpion changed their clear blue colour to dark dusty blue and sometimes brownish blue but not to brown colour as it ought to be if all inulin was converted into fructose.

This experiment was repeated five times with the same results. A small amount of inulin has been converted into fructose.

7. Amylase

Amylase is capable of converting starch to maltose. The presence of an insignificant amount of Amylase in the scorpion was established by Krukenberg, by Fischer, and by Kobert, and later by Pavlovsky and Zarin.

METHOD

For the detection of Amylase we used .3% and .5% solutions of soluble starch (amyl. solubile) and an aqueous solution of iodine in potassium iodide.

.3 gm. and .5 gm. of soluble starch were separately dissolved in 100 c.cs. of hot distilled water each. The solutions were then allowed to cool and were filtered in separate bottles. 2 c.cs. each of the glycerine extracts of the liver, the stomach glands and the mid-gut of the scorpion were taken in three different test tubes and in a fourth one 2 c.cs. of pure glycerine were taken as a control solution. To each of these four tubes were added 8 c.cs. of distilled water and .5 c.cs. of the .5% solution of starch. Similarly, four other test tubes were prepared with the .3% starch solution.

Thus altogether eight test tubes were prepared. After vigorously shaking them, they were all kept in a water bath at 40°—45°c. for 30 minutes after which they were allowed to cool. 2 c.cs. of the contents of each tube were taken out in smaller tubes and to each of them 3 drops of an aqueous solution of iodine in potassium iodide were added.

RESULTS

It is known that in the presence of Amylase, starch is converted into maltose, on being heated. Therefore when treated with iodine solution it does not give a deep blue colour reaction.

Control :—In both the control test tubes (with .3% and .5% starch) a deep blue colour was obtained on addition of 3 drops of iodine.

Liver and Stomach glands :—In the test tubes containing the extracts of liver and stomach glands, the solutions with the .5% starch gave a dusty pink colour reaction with a slight bluish tinge, while the solutions with the .3% starch gave an absolute pink colour without any trace of blue, on the addition of 3 drops of iodine. This indicates that the .5% starch remained partly unchanged while the .3% starch completely disappeared.

Mid-gut :—In both the test tubes containing the extract of mid-gut (with .3% and .5% starch) a dark purple colour was obtained on the addition of 3 drops of iodine, thus indicating that the mid-gut contains no Amylase strong enough to convert the starch into maltose.

TIME FACTOR

In the above experiments the time allowed for the Amylase in the extracts to act on the starch was generally 30 minutes. However, in order to determine the time necessary for the conversion of starch into maltose by the Amylase of the extracts, several experiments were performed when the solutions were tested at intervals of every 5 minutes. The results are noted in the following table :—

TABLE OF EXPERIMENTS SHOWING THE TIME TAKEN BY AMYLASE TO ACT ON STARCH

Time	Control	Mid-gut	St. Glands	Liver	More Concentrated Liver
0 mts.	Clear dark blue	Dusty dark blue	Dusty dark blue	Dusty dark blue	Dusty dark blue
5 mts.	,,	,,	Dusty purple	Dusty purple	Dusty light purple
10 mts.	,,	Dusty purple	Dusty light purple	Dusty light purple	Dusty pink with blue
15 mts.	,,	,,	Dusty pink with blue tinge	Dusty pink with blue tinge	Dusty pink

The solutions used in the above experiments were prepared with 5% starch only. 2 c.cs. of each solution were tested in the beginning of the experiment with 3 drops of iodine, and then 2 c. cs. at intervals of every 5 minutes, till no reaction was noticed. It will be seen from the above table that the more concentrated extract of liver acted on the starch quicker than the less concentrated solutions, indicating that it contained naturally a larger quantity of the enzyme Amylase. The "dusty" colour of the solutions was due to the colour of the extracts.

CONCLUSION

From all the above experiments it may be concluded that Amylase is present in equal strength in both the liver and the stomach glands of the scorpion. The more concentrated the extract, the more quickly it acts on the starch. In the mid-gut, however, the presence of Amylase cannot be certain. The tissue is so small and thin that the extract was naturally more dilute than that of the liver or the stomach glands. Consequently its action on the starch, if any, could not be easily noticed. The slight changes effected by the starch in the mid-gut solutions in all the experiments indicate that Amylase might have been present. It is possible on the other hand that this slight trace of the ferment had come from the liver into the mid-gut during digestion and had not originated there.

Pavlovsky and Zarin were able to establish the presence of Amylase only in the extract of the liver, and in all their experiments with the extracts of the stomach glands and the mid-gut they obtained negative results. It may be that these latter extracts they used were too dilute to give any results. In all our experiments the extracts of the liver and the stomach glands both acted equally on starch.

8. **Catalase**

Catalase is capable of decomposing hydrogen peroxide into molecular oxygen and water :—

$$2H_2O_2 = O_2 + 2H_2O$$

The catalytic properties of some animal and plant tissues were established by Schonbein in 1863. More detailed investigations on the ferment Catalase were published by Loew in 1901.. The Catalase of scorpions was studied by Kobert in 1913, but he obtained negative results He, however, worked on specimens preserved in 70% alcohol for more than 5 years. Pavlovsky and Zarin in 1926 established the presence of Catalase in the liver of Buthus.

METHOD

For our experiments we constructed an apparatus similar to the one described by Zarin (1913).

This apparatus consisted of a broad-mouthed glass bottle with a rubber stopper, an S-shaped tube, a water trough, and a graduated test-tube. The apparatus was fitted up as shown in Figure 2.

2 c.cs. of the glycerine extract of the liver of scorpion were mixed with 8 c.cs. of distilled water. The mixture was filtered through filter-paper into the bottle (B). To this were added 10 c.cs. of 1% solution of hydrogen peroxide prepared from Merkozone. (1 c.c. of Merkozone plus 7 c.cs. of distilled water as Merkozone itself is 8% H_2O_2). The bottle was immediately corked with the rubber stopper (C) containing the S-tube (S.T.). The distal end of the S-tube was quickly inserted, under water, into the inverted graduated test tube (C) which was full of water.

Effervescence began to take place as soon as H_2O_2 was added to the liver extract, and small bubbles of gas were seen to collect in the graduated test tube displacing the water therein. The apparatus was allowed to remain for 24 hours and sometimes for a longer period.

The above experiment was performed also with the glycerine extract of the stomach glands of scorpion, and as a control with only pure glycerine instead of the extracts.

RESULTS

Control :—With the control solution there was no evolution of any gas and the test tube remained completely full of water throughout the experiment.

Liver extract :—9 experiments were performed with the glycerine extract of liver and of these 6 gave positive results. The quantity of O_2 evolved, however, varied.

9 more experiments were performed with the more concentrated extract of the liver. 8 of these gave positive results and the quantity of the O_2 evolved varied as in the above case.

Stomach glands extract :—With the glycerine extract of the stomach glands 5 experiments were performed of which 4 gave positive results. The quantity of O_2 evolved varied in this also.

The variation in the quantity of the oxygen evolved, and the negative results in a few cases (5 out of 23 experiments) were unaccountable. But the fact that Oxygen did evolve in the majority of cases is only of importance as it proves the presence of the ferment Catalase in both the liver and the stomach glands.

Pavlovsky and Zarin performed only three experiments with the liver extract and three with the stomach glands extract. Only in one experiment they detected the evolution of Oxygen, and that in the case of the liver extract. All their experiments with the stomach glands extract gave negative results.

TESTING THE GAS

In order to test the gas evolved, a larger quantity of the more concentrated extract of the liver was taken in a big bottle and to this a proportionately larger quantity of strong solution of hydrogen peroxide was added. The bottle was then at once tightly closed and was allowed to remain for about 50 minutes. Afterwards the stopper was lifted and a kindling stick of wood was immediately inserted. The stick caught fire and began to burn brightly. Several times the experiment was repeated with the same results. This proves that the gas evolved was undoubtedly Oxygen.

With only glycerine, sand, and hydrogen peroxide (without any extract) this test was made as a control, but there was no evolution of gas.

TABLE SHOWING A SUMMARY OF THE EXPERIMENTS

Ferments Tested	Number of Experiments Performed	Results	Remarks
Chymosin	5 Liver extract	Positive	
	5 Stomach glands	,,	
Pepsin	7 Liver	,,	30% gelatin used
	7 Stomach glands	,,	,, ,,
	6 Liver	(Gelatin did not set)	10 to 25% ,, gelatin used
	6 Stomach glands		
Trypsin	*Neutral gelatin*		
	4 Liver	Positive	30% gelatin used
	4 Stomach glands	,,	,, ,,
	2 Liver	(Gelatin did not set).	15% and 25% ,, gelatin used
	2 Stomach glands	,,	,, ,,
	Alkaline gelatin		
	7 Liver	Positive	30% gelatin used
	7 Stomach glands	,,	,, ,,
	4 Liver	(Gelatin did not set)	15 to 25% gelatin used
	4 Stomach glands		
	Casein Test		
	4 Liver	Positive	
	6 Stomach glands	,,	
Invertase	2 Liver	Negative	
	2 Stomach glands	,,	
Lipase	2 Liver	Positive	
	2 Stomach glands	,,	
Inulase	5 Liver extract	,,	
	5 Stomach glands	,,	
Amylase	*In water bath (40°-45°c)*		
	4 Liver	Positive	
	4 Stomach glands	,,	
	At room temperature (about 30°c)		
	3 Liver	Positive	
	3 Stomach glands	,,	
	In water bath (70°-80°c)		
	1 Liver	Negative	Overheated
	1 Stomach glands	,,	Control even gave no reaction with iodine
Catalase	14 Liver	Positive	
	4 ,,	Negative	Unaccountable
	4 Stomach glands	Positive	
	1 ,, ,,	Negative	Unaccountable

HISTOLOGICAL STUDY OF THE DIGESTIVE GLANDS

For the structural study of the liver and the so-called stomach glands of the scorpion, tissues of these organs were fixed in Bouin's Picro-Formol for about 24 hours. Then, in order to remove the colour of the picric acid from the tissues, they were washed in a solution of lithium carbonate and again in water. Paraffin sections 10 μ in thickness were cut and double stained in hæmatoxylin (Delafield's) and eosin.

THE LIVER

The sections of the liver (Fig. 3) reveal the presence of two kinds of cells. The cells of the first kind (A.C.) are larger and occupy a greater portion of the liver tissue. They have large oval nuclei which are stained dark blue in haematoxylin. The cells are overladen with numerous large globular inclusions (Gl.) of different sizes. These are stained in different tints of violet. The cells also contain small granular inclusions (Gr.) disposed in groups. They stain brownish black. Cells of this type were found by Pavlovsky and Zarin in the liver of Buthus. They have called them "absorption cells" or "resorption cells" as they are believed to absorb digested food material.

The cells of the second kind (F.C.) are fewer than the other and are filled with a large amount of fine granular substance which stains light pink. Pavlovsky and Zarin have described such cells in the liver of Buthus and have called them "ferment cells" being responsible for the secretion of the various ferments.

The liver is bounded by a peritonial membrane (M.) which is made up of large poligonal cells with large oval nuclei. This membrane penetrates the liver tissue at different places thus dividing the liver into small lobules. In this membrane are found here and there large blood lacunae (B.L.) and there ramify also the so-called Malpighian vessels (M.V.). In the cells of this peritonial membrane are also encountered globular inclusions (G.l.) similar to those of the absorption cells.

THE STOMACH GLANDS

The sections of the so-called stomach glands (Fig. 4) also show two kinds of cells corresponding to the absorption cells and ferment cells of the liver with their identical inclusions, and the whole gland is clothed with a peritonial membrane which, as in the case of the liver, penetrates the tissues and divides the stomach glands into many small lobules. The membrane also contains a few blood lacunae and Malpighian vessels. In all respects therefore the cells of the stomach glands are similar to those of the liver.

Histological study therefore proves that the liver and the stomach glands are structurally identical In this conclusion, we have the support of Pavlovsky and Zarin whose description of the structures of these glands of Buthus compares favorably with that of ours. The conclusion arrived at by Pavlovsky and Zarin, however, is the more significant on account of the fact that their physiological studies on the enzymes of these organs led them to conclude differently.

CONCLUSION

The main digestive gland of the scorpion consists of 5 pairs of glands collectively called the 'liver' or 'hepato-pancreas', and it occupies a large portion of the body cavity of the mesosoma. In front of this, lying in the pro-soma, is a pair of glands, very small, but in appearance similar to the liver. This little pair of glands has been called the 'salivary glands', the 'cephalo-thoracic outgrowth of the liver', the 'stomach glands', etc., by different authors. Whether these so-called stomach glands are distinct from the liver or are only cephalo-thoracic outgrowths of the liver was the problem which attracted the attention of Pavlovsky and Zarin in 1926. They made separate glycerine extracts of the liver and the stomach glands of Buthus and tested these extracts for their enzyme contents. The extract of the liver revealed to them the existence of the ferments Chymosin, Pepsin, Trypsin, Lipase, Amylase and Catalase in them. In the extract of the stomach glands, Amylase and Catalase were not found. The ferments Lipase and Chymosin were detected only once in the stomach glands extract, while they were present in those of the liver in every one of the three experiments they performed. From these results, Pavlovsky and Zarin concluded that the two sets of glands were physiologically different. They also studied the histology of these glands and found that in histological structure the stomach glands agreed with the liver. This feature, however, did not preclude them from arriving at the aforesaid conclusion.

Our experiments were conducted on the digestive glands of the scorpion *Palamnaeus fulvipes*, on the same lines. All the ferments found by by Pavlovsky and Zarin in the liver of Buthus, viz. Chymosin, Pepsin, Trypsin, Lipase, Amylase and Catalase, were found by us in the liver as well as in the stomach glands of Palamnaeus. That means that the two ferments Amylase and Catalase which were not detected by Pavlovsky and Zarin in the stomach glands, and the two ferments Lipase and Chymosin which they detected only once in the stomach glands, were found present in all our extracts of the stomach glands tested. Moreover we found traces of inulase in both the glands. We give below a comparative table of the results obtained by Pavlovsky and Zarin and those obtained by us.

TABLE COMPARING OUR RESULTS WITH THOSE OF PAVLOVSKY AND ZARIN

Ferments Investigated	*Pavlovsky and Zarin*		*Bardi and George*	
	Liver	St. Glands	Liver	St. Glands
Chymosin	*Present* in all 3 exps. Result after 10 mts.	*Present* in one expt. only. Result after 50 mts. *Absent* in 2 other exps.	*Present* Results obtained in both glands after 10 minutes in all 5 experiments.	*Present*
Pepsin	*Present* in all 3 exps. Liquefaction of gelatin commenced after 2 days.	*Present*	*Present* Liquefaction of gelatin commenced after a few minutes, with both glands in all 7 exps.	*Present*

Table Comparing our Results with those of Pavlovsky and Zarin—(*contd.*)

Ferments Investigated	*Pavlovsky and Zarin*		*Bardi and George*	
	Liver	St. Glands	Liver	St. Glands
Trypsin	(Gelatin Test) *Present* in all 3 experiments	*Present*	(Gelatin Test) *Present* in all 11 experiments	*Present*
	(Casein Test) *Present* in all 3 exps.	*Absent* in all 3 exps.	(Casein Test) *Present* in all 4 experiments	*Present*
Invertase	*Absent* in all 3 experiments	*Absent*	*Absent* in all 2 experiments.	*Absent*
Lipase	*Present* in all 3 exps.	*Present* only in one exp. *Absent* in 2 others	*Present* in all 2 experiments	*Present*
Inulase	*Absent* in all 3 experiments	*Absent*	*Present* in all 5 experiments	*Present*
Amylase	*Present* in all 3 exps.	*Absent* in all 3 exps.	*Present* in all 7 experiments	*Present*
Catalase	*Present* only in the 1st exp. *Absent* in 2 others	*Absent* in all 3 exps.	*Present* in 14 out of 18 exps.	*Present* in 4 out of 5 experiments

From the above Table it will be clear that our experiments show no difference between the so-called stomach glands and the liver as regard their enzyme contents.

We have also made a histological study of these organs and we agree with Pavlovsky and Zarin that structurally these two glands are similar.

From our investigation, therefore, it appears that the so-called distinction into stomach glands and liver has neither histological nor physiological foundation. The former must, therefore, be regarded as a part of the hepatopancreatic system, being the anteriormost pair of the several pairs of glands, having remained separate, however, as a result of the development of the endosternite which separates the prosoma from the mesosoma.

ACKNOWLEDGEMENT

Before concluding this paper we wish to express our gratitude to Dr. S. C. Devadatta for many valuable suggestions.

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EXPLANATION OF THE PLATES

FIGURE 1. *Dissection of the scorpion to show the digestive glands in position.*

H.P.	The five pairs of liver glands (hepato-pancreas) opening into the mid-gut.
M.G.	Mid-gut.
M.S.	Meso-soma.
P.S.	Pro-soma.
S.G.	The anteriormost pair of liver glands (the so-called stomach glands) opening into the stomach.
St.	Stomach.

FIGURE 2. *An apparatus for the estimation of catalase (After Zarin).*

B.	Bottle with extract plus hydrogen-peroxide sol.
C.	Rubber stopper through which an S-tube passes into the bottle.
E.	Glycerine extract of the digestive gland plus hydrogen-peroxide solution.
	Graduated test tube for receiving the oxygen evolved.
H_2O	Water filling the trough and the test tube.
O_2	Oxygen collected in the test tube.
S.	Stand for holding test tube in position.
S.T.	S-shaped tube.
T.	Trough filled with water.

FIGURE 3. *A part of the section of a lobe of the liver* (oc.3 × ob. 3).

A.C.	Absorption cells.
B.L.	Blood lacunae.
F.C.	Ferment Cells, with granular substance.
Gl.	Globular inclusions.
Gr.	Granular inclusions.
M.	Membrane.
M.V.	Malpighian Vessels.

FIGURE 4. *A part of the section of a lobe of the so-called stomach glands* (oc.3 × ob. 3) (Letterings as in Figure 3).

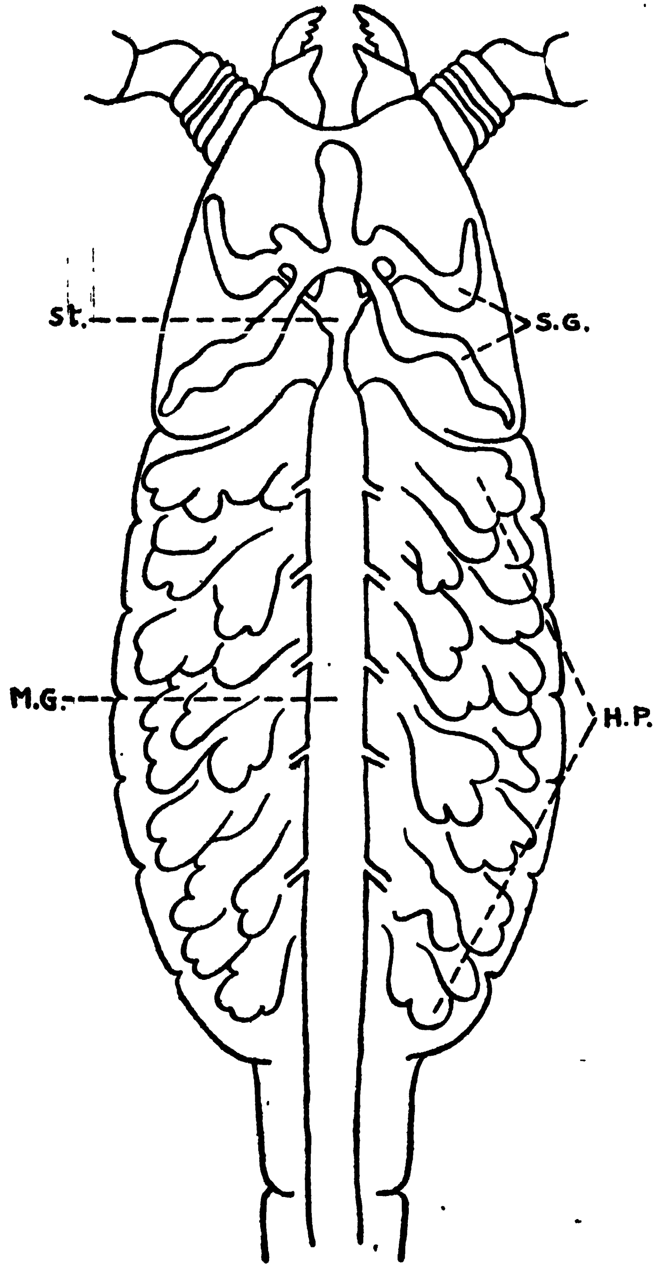

Fig. 1

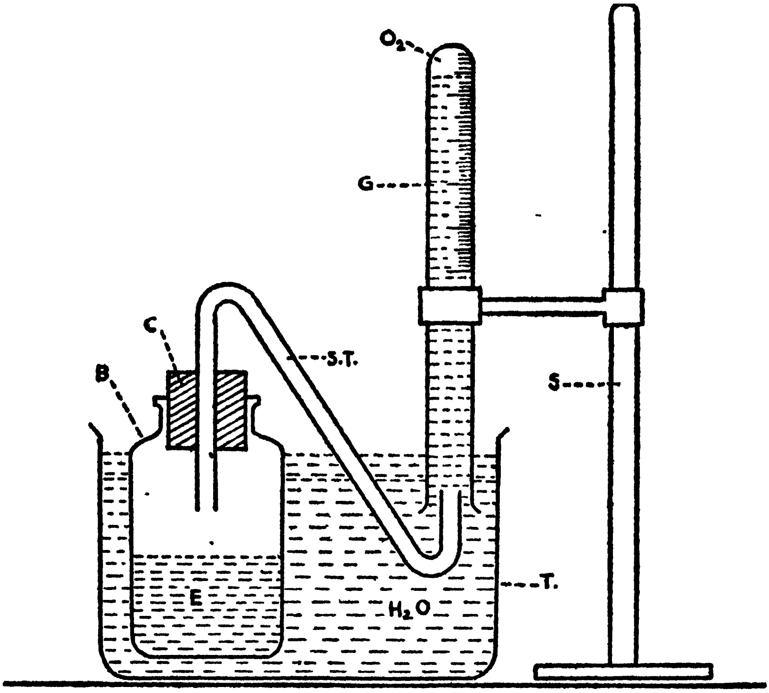

Fig. 2

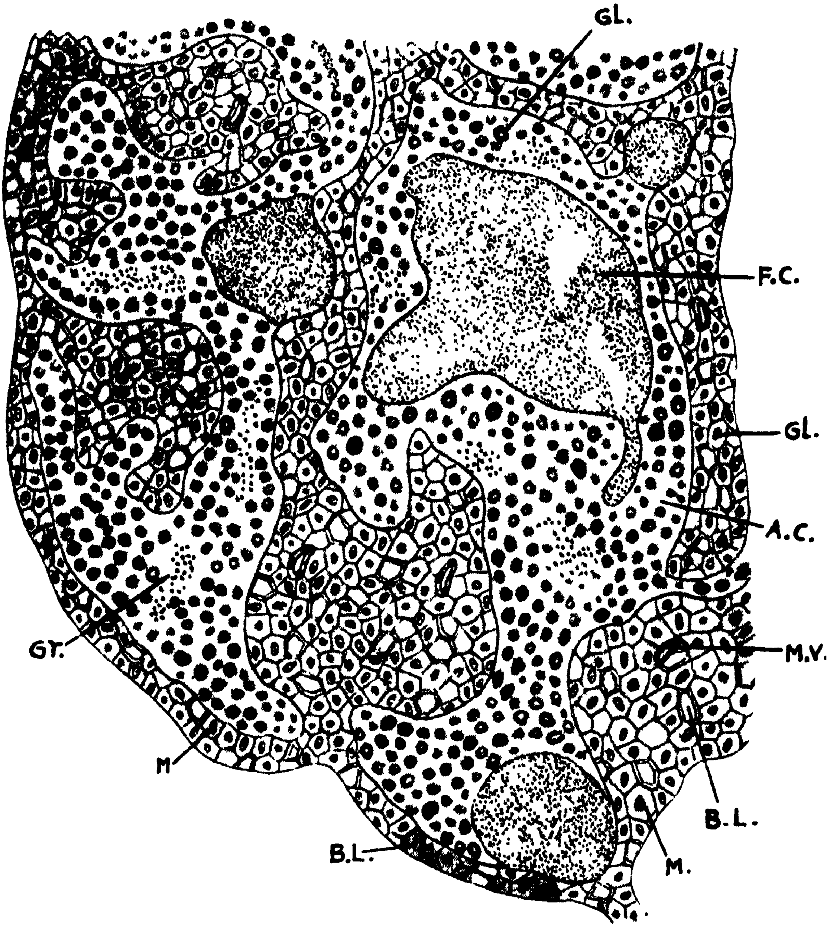

Fig. 3

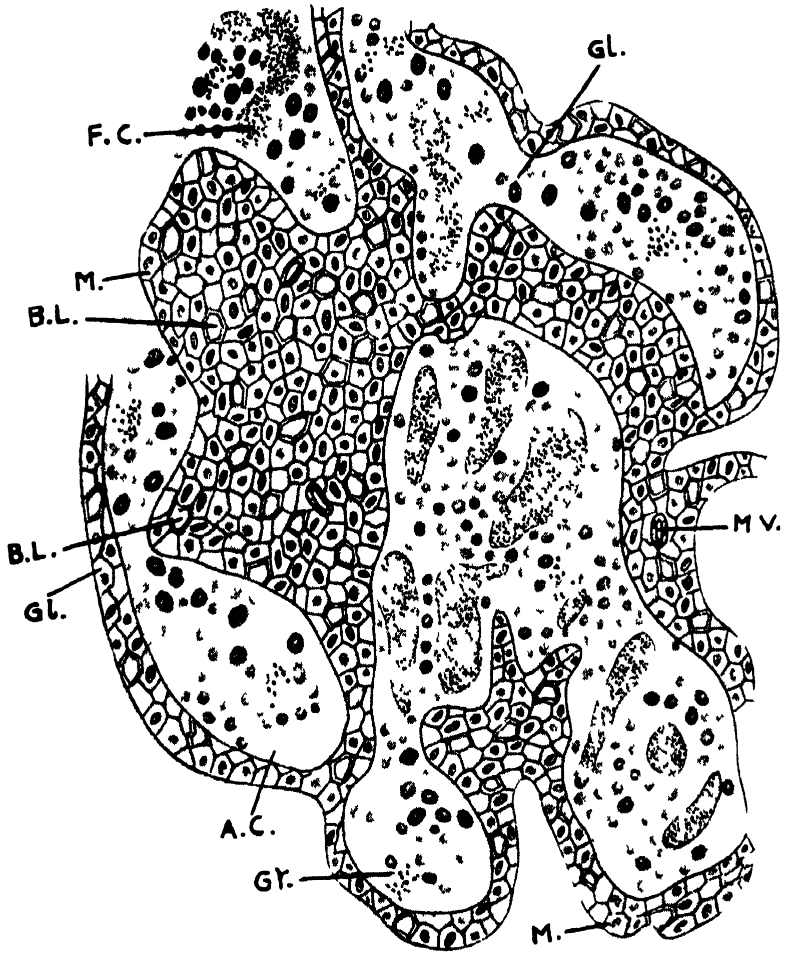

Fig 4

STUDIES IN THE DEVELOPMENT OF SEED CHARACTERS IN LINSEED

(*Linum usitatissimum*)

By

L. S. S. KUMAR AND D. S. RANGA RAO,

Department of Botany, College of Agriculture, Poona

BREEDING work for the improvement of linseed has been in progress in the Bombay Province for the last nine years and advantage was taken of this opportunity to study the physical and chemical characters of linseed at progressive stages of maturity. The authors are not aware of any reference to such work in India using the local varieties of linseed grown under Indian conditions.

Dillman (1928) and Eyre (1931) studied the daily growth and oil development in flax-seed. Barker (1932) in Great Britain investigated the nature and quantity of oil in seeds of flax-fibre crop at successive stages of maturity. The relation of agronomic practice to the quantity and quality of oil in flax-seed was studied by Johnson (1932). Lehberg *et al.* (1939) have studied the physical and chemical characteristics at various stages of maturity of the seeds of three varieties of flax most extensively grown in Canada. The present work includes the study of the physical characteristics of the capsule and seeds, the germination percentage of the seeds, oil content and iodine value of the oil from the earliest stages to complete maturity of the seeds in an Indian variety of linseed under local conditions at Poona.

MATERIAL

A pure strain—C.P. 3—obtained from the Central Provinces and acclimatised to local conditions for three years was selected as suitable material for these studies. The crop was grown by dibbling during the *rabi* season on a typical medium black clayey loam soil of the experimental plots of the Economic Botanist at the Poona Agricultural College. Throughout the period of growth the crop was neither manured nor irrigated. The studies were conducted during the *rabi* seasons of two years 1936-37 and 1939-40. Data are presented only for the latter period, as during that year more characters were studied and the results were statistically analysed. But the trend of the results for the characters studied during both years was found to be the same.

METHODS

About nine weeks after sowing, when sufficient number of flowers were available, 1200 freshly opened flowers were labelled with tags on the same day. Thereafter, weekly samples of 100 capsules each were taken at random at about 1 p.m. each time. The samples were allowed to sun dry till the evening and stored in butter paper bags for further work in the laboratory.

Physical characters.—Each capsule was separately weighed and its size measured by taking the maximum width by means of calipers with vernier attachment. After determining the number and weight of seeds in each capsule, the seeds from the hundred capsules at each stage of maturity were well mixed and 100 seeds of this lot were used to determine their average length, breadth and thickness.

Germination percentage.—Two lots of fifty seeds from each sample were allowed to germinate on moist blotting paper in shallow dishes. Counts were taken when radicles had come out and cotyledons had just made their appearance.

Oil content.—Duplicate 1 gm. samples at each stage of maturity were ground, and extracted with ether. The extract was dried for an hour at 60°C in an electric oven and for another hour under vacuum in a desiccator over calcium chloride and weighed. By employing the above method, the difference between duplicates was never over 0.5 per cent.

Iodine value.—This was determined in the above oils by the method of Hanus (Methods of the Association of Agricultural Chemists, U.S.A., 1938).

TABLE I

Development of seed characters at progressive stages of maturity

(The figures given in the table are average values)

Date of Sowing 11-10-39.
Date of Tagging 18-12-39.

Date of harvest	Age of capsule in days	Germination	Size of capsule maximum width	No. of seeds in a capsule	Weight of single capsule	Weight of single seed	Length of seed	Breadth of seed	Thickness of seed	Oil	Iodine value	General appearance of seed
		per cent	mm.		mg.	mg.	mm.	mm.	mm.	per cent		
25-12-39	7	..	5.151	5.635	20.228	0.710	3.545	1.733	0.2815	..	..	Seeds green, membranous & shrivelled.
1-1-40	14	15	*8.285*	*8.210*	*34.980*	*1.930*	*5.195*	*2.721*	*0.5830*	20.01	142.35	Membranous & transparent.
8-1-40	21	56	8.*753*	8.280	*59.850*	*4.695*	5.191	*2.790*	*0.8450*	33.98	168.40	Larger than previous lot, colour that of matured seed.
15-1-40	28	93	8.860	8.640	*78.750*	*6.695*	*5.424*	2.816	*1.023*	38.96	165.76	Size, shape, colour, like that of fully matured seed.
22-1-40	35	95	8.888	8.170	*88.450*	*8.035*	*5.492*	2.806	*1.272*	39.99	171.07	
29-1-40	42	94	8.878	8.190	91.100	*8.485*	5.507	*2.777*	*1.338*	40.24	172.05	
5-2-40	49	94	*8.988*	8.240	87.220	8.165	5.520	2.799	1.303	38.86	166.25	
12-2-40	56	99	8.985	8.350	89.600	8.295	*5.477*	2.780	1.321	38.78	168.42	
19-2-40	63	94	8.965	7.810	*78.760*	*7.665*	5.502	*2.754*	1.288	38.87	170.00	

(Figures in *italics* indicate that they are statistically significant with respect to the previous figure.)

RESULTS AND DISCUSSIONS

Each of the physical characters was statistically analysed by finding out the mean, standard deviation and standard error for the values at each stage of development. The difference in mean values between any two stages was considered significant when it was more than twice the standard error of difference between the two means. The results are summarised in Table I wherein the figures represent merely the average values. Wherever the results are statistically significant, such figures are shown in italics in the table.

Size of capsules.—This rises very rapidly in the first two weeks, after which the rise is very slow. After reaching the maximum during the seventh week, the size remains the same without any further decrease. Both Dillman (1928) and Johnson (1932), however, find that the size of

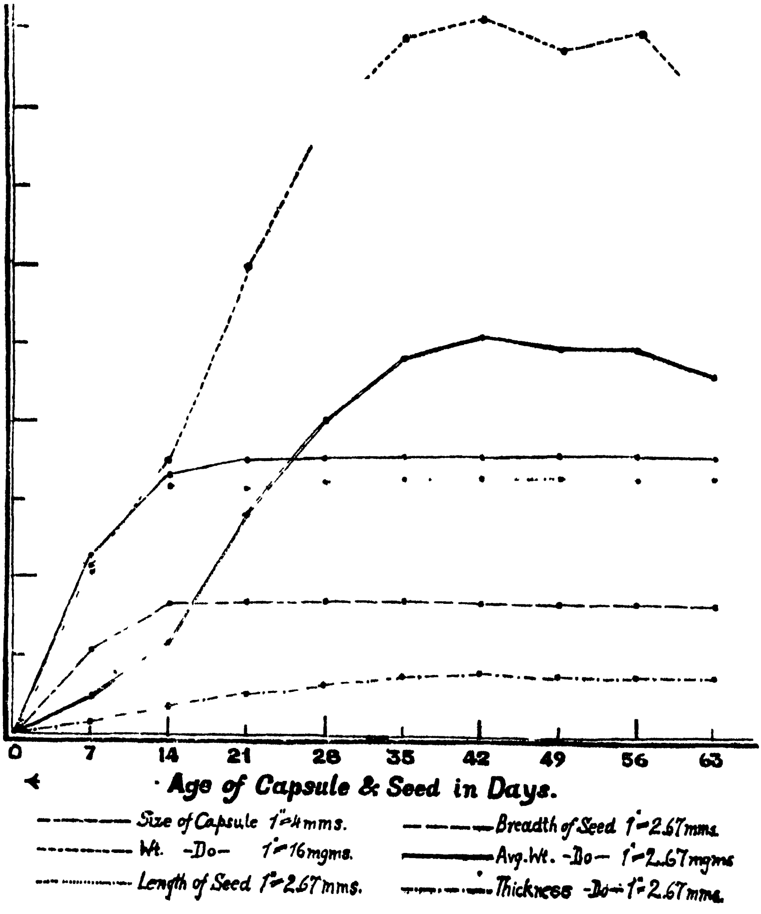

Fig. 1.

Graph illustrating development of physical characters at progressive stages of maturity in linseed capsule reaches maximum size of the development within two weeks after flowering, remains stationary over a considerable period and then registers a slight decrease during the ripening stage of the crop. This decrease in the final stages was not observed in the present work.

Number of seeds per capsule.—By the end of the first week, the average number of seeds per capsule was between 5 and 6 only. But by the end of the second week, this rose to about 8 per capsule which was the maximum obtained. This variation in setting of seeds during different stages of development has not been reported by other workers.

Weight of capsule and seed.—The trend of results in these two cases runs parallel as can be seen in the curves in the graphs in Fig. 1. Both show a sharp and steady rise during the first five weeks, reach their maximum during the sixth week, and remain at that level with slight fluctuations till the end of the eighth week, and then show a fall during the ninth week. This fall in the last week has been found to be statistically significant.

Length, breadth and thickness of seed.—Dillman (1928) and Johnson (1932) have observed that these three values show parallel development. They reach maximum within two weeks after flowering, remain fairly constant over a considerable period, and all the three decrease slightly at complete maturity. In the present studies also it was noticed that all these three characteristics register a very rapid rise in the first two weeks. But the further development in each case was not similar to that observed by Dillman (1928) and Johnson (1932). The length of the seed reaches the maximum only during the fifth week and shows a decline during the eighth week. The breadth reaches the maximum during the third week itself and decreases during the ninth week. In both cases, the decreases are significant. The thickness of seed, however, rises very gradually to reach a maximum by the end of the sixth week. But unlike the length and breadth of the seed, the thickness does not show any decrease at all.

Oil content.—There is a fairly rapid accumulation of oil even from the earliest stages. More than 80 per cent of the maximum oil content is formed by the end of the third week. The rate of increase in oil content becomes almost negligible after the fourth week, and the maximum oil content is reached by the end of the sixth week when the average capsule and seed weights also reach their maximum. Thus the oil formation runs concurrent with the formation of dry matter in seed and capsule (*vide* Graph in Fig. 1). This point is reached some 7 to 10 days before the crop is usually harvested. More or less similar observations on the rate of development of oil in the seed have been made by Dillman (1928), Barker (1932), Johnson (1932), Eyre (1931) and Lehberg (1939), but only Johnson has observed the diminution of oil content in the final stages of maturity. As can be seen from Table 1, here, also, a similar lowering of the oil content is noticeable after the sixth week.

Iodine value.—Just as in the case of oil content there is a rapid increase in iodine value of the oil in early stages. The rate of increase in iodine value is almost similar to that of oil content itself. Both reach their maximum by about the same time, *viz.*, by the end of sixth week. Johnson (1932) has observed similar phenomena and states that the iodine value increased rapidly in 5 to 17 days, but Barker (1931) as well as Lehberg (1939) find that the greatest rate of increase in iodine value takes place after the oil content has reached its maximum value. According to them, change

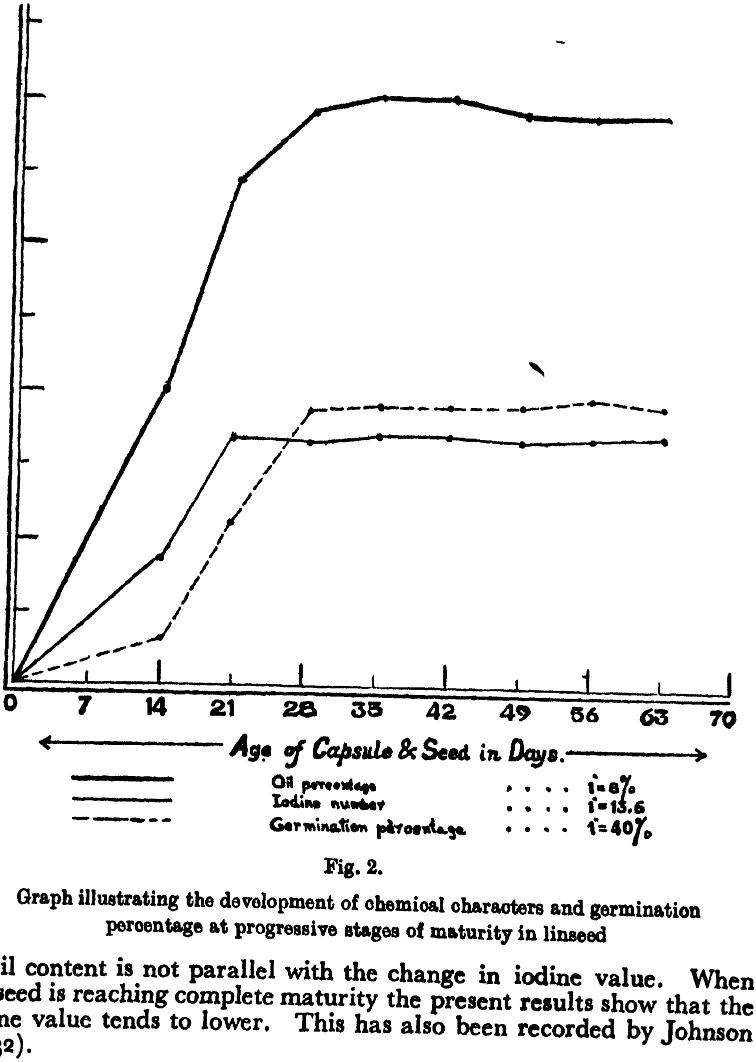

Fig. 2.

Graph illustrating the development of chemical characters and germination percentage at progressive stages of maturity in linseed

in oil content is not parallel with the change in iodine value. When the seed is reaching complete maturity the present results show that the iodine value tends to lower. This has also been recorded by Johnson (1932).

Germination percentage.—At the end of the first week, the seed appears green, membranous and shrivelled and is incapable of germination. Two weeks' old seeds are still membranous and transparent and give 15 per cent germination. After the third week onwards, the seed looks well matured and there is more than 90 per cent germination. These results are in the main in agreement with those of Dillman (1928) except that in his experiment there were higher percentages of germination in the earlier stages. He obtained 38 and 80 per cent germination in seeds of 15 and 18 days old respectively.

From the above studies it can be seen that the economic characters—yield, oil content, and quality of the oil—all reach their maximum development by the end of the sixth week after flowering. At this stage the capsules will have attained a very light brown colour. The usual local practice of harvesting is to wait for another 7 to 10 days when capsules develop a brown colour of a much darker tint. The present work shows that during this period there is an actual decrease in yield, oil content and also iodine value of the oil. It may thus be advantageous to harvest the crop a week to ten days earlier than what is being practised commonly.

SUMMARY

The development of physical and chemical characteristics at different stages of maturity of the seeds of a pure strain—C. P. 3—of linseed from the Central Provinces has been studied.

Percentage germination, length, breadth, thickness and weight of seed, size of capsules, oil content and iodine value of the oil have been investigated in weekly samples of seed from flowering to maturity. During the first week of flowering on an average only about 5 seeds are set per capsule. In another week the number of seeds in a capsule increases to about 8 which is possibly the maximum obtainable under field conditions.

Average weight of capsule, average weight of seed, oil content and iodine value of the oil, all show an almost parallel development. The maximum values in these cases are reached by about the end of the sixth week, after which they all show a slight decrease towards the final stage of maturity.

Hence it is suggested that it is economically advantageous to harvest the crop about a week earlier than is usually the practice in the country.

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THE ALGAL FLORA OF TEMPORARY WATERS AROUND BOMBAY

II. A Study of the Algae in some Rain-water Puddles at Jogeshwari

By

Ella A. Gonzalves, B.A., M.Sc.,

and

Dwarka B. Joshi, M.Sc.,

Botany Department, Royal Institute of Science, Bombay

IN the previous paper of this series the algae of a group of rain-water pools at Borivli were studied. In order to understand more thoroughly the factors that cause, modify and direct the growth of freshwater algae around Bombay, it is necessary to repeat these investigations on numerous other waters in the locality. In this way a wealth of data will be accumulated which will lead to a determination of the ecological factors influencing the algae in small bodies of water. The second group chosen for study was a small collection of rain-water puddles situated inside the Jogeshwari Caves. Jogeshwari is about 17 miles north of Bombay and the caves are about ½ mile to the east of the railway station. They consist of a central hall, in the middle of which is a shrine, and extensive wings. Parts of the top portion of the side wings have fallen in, and so these halls are exposed to sunlight. Rain-water collects on the ground forming puddles scarcely three to six inches deep. A collection was made from this spot and as it contained a large number of desmids, it was thought advisable to make systematic collections throughout the monsoon and to study the algal flora, just as in the case of the Borivli pools (*cf.* Part 1). The collections were made once a fortnightduring the monsoon of 1940. The species were identified and the frequencies were noted according to the system of Howland (*cf.* Part 1). The meteorological data for 1940 are also given in the first part of this series.

THE ALGAL FLORA OF THE POOLS

The following is a list of the forms observed in the pools :—

I. CHLOROPHYCEAE (ISOKONTAE)*

CHLOROCOCCALES 1) *Scenedesmus obliquus* (Turpin) Kütz., 2) *S. brasiliensis* Bohlin., 3) *S. bijugatus* (Turp.) Kütz. var. *alternans* Reinsch., 4) *Coelastrum cambricum* Archer.

ULOTRICHALES 5) *Ulothrix tenerrima* Kütz.

OEDOGONIALES 6) *Oedogonium hirnii* Gutw., 7) *Oe. ahlstrandii* Wittr.

CONJUGALES 8) *Spirogyra* sp.,† 9) *S. Kuusamoensis* Hirn, 10) *Closterium acerosum* (Schr.) Ehr., 11) *C. Dianae* Ehr forma, 12) *C. moniliferum* (Bory) Ehr., 13) *Cosmarium polygonum* (Näg) Arch., 14) *C. binum* Nordst., 15) *C. Quadrum* Lund., 16) *C. connatum* Bréb., 17) *C. vexatum* West., 18) *C. asphaerosporum* Nordst., 19) *Staurastrum Zahlbruckneri* Lutkem forma Krieger., 20) *Micrasterias denticulata* Bréb., 21) *Desmidium Swartzii* Ag., 22) *Penium cucurbitinum* Biss., 23) *Cylindrocystis crassa* De Bary.

II EUGLENINEAE

24) *Euglena proxima* Ehr., 25) *Trachelomonas volvocina* Ehr.

III MYXOPHYCEAE (CYANOPHYCEAE)

26) *Lyngbya cryptovaginata* and 27) *Coelosphaerium Nägelianum* Unger.

Most of the species in these pools belonged to the Conjugales and to the desmids in particular. The other orders had very few representatives. There were very few members of the Cyanophyceae even at the end of the season. Table I gives the frequency of a few of the forms during the season.

TABLE I

	June 24	July 9	July 27	Aug. 10	Aug. 24	Sept. 2	Sept. 21	Oct. 4
1. *Scenedesmus obliquus*	i	c	c	a	rc	r	vr	i
2. *Oedogonium ahlstrandii*		rc	c	c	! a	rc	r	
3. *Spirogyra Kuusamoensis*	i	vr	rc	a	! a	c	rc	vr
4. *Closterium moniliferum*	rc	rc	c	rc	rc	rc	rc	r
5. *Cosmarium polygonum*	rc	rc	a	a	rc	rc		
6. *Micrasterias denticulata*			r	a	a	rc	r	
7. *Lyngbya cryptovaginata*	r	vr			r	c	a	rc

! *denotes sexual reproduction.*

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*The classification adopted is that of Fritsch in "The Structure and Reproduction of the Algae"—1935.

† This appears to be a new species of Spirogyra, and will be described in a subsequent paper.

CONSIDERATION OF THE ALGAE

CHLOROCOCCALES: All the three species of *Scenedesmus* were seen throughout the season, but *S. obliquus* was the only species seen in the first collection. All three showed appreciable increase in July and continued so till the end of August, the maximum being reached about the end of July. From September onwards, they were rare.

ULOTRICHALES: *Ulothrix tenerrima* was the only member of this order. It occurred in the beginning of August and was seen till the end of September. It was never in abundance but became more scarce at the end of September.

OEDOGONIALES: Two species of *Oedogonium*, *viz.*, *Oe. ahlstrandii* and *Oe. hirnii* were seen. The latter was present throughout the season. It appeared in the third week of July and became abundant in the beginning of September when the maximum was reached. Oogonia were formed in late August. *Oe. hirnii* appeared much later, *i.e.*, in the beginning of September. It was never in abundance. Only a few fruiting filaments were observed.

CONJUGALES: Of the two species of *Spirogyra*, *S. Kussamoensis* was seen throughout the season. It became abundant in the first half of August, remained so till a fortnight later when zygospores were formed, and then declined. The other species of Spirogyra was seen towards the end of July. It reached its maximum by the end of August and formed zygospores in the beginning of September.

Of the desmids, *Closterium moniliferum* occurred at the beginning of the season and reached its maximum at the end of July. Though this form was seen throughout the season, it was never in abundance. The other two species of *Closterium* though they appeared for a shorter period, *viz.*, from the beginning of July till the end of August, were seen in larger amount. The occurrence of desmids and of *Closterium acerosum* in particular, in a shallow pool is not unexpected, as Hodgetts (1921) found *Closterium acerosum* thriving best in very shallow water at the margin of a pond. All the other desmids appeared by the middle of July. But only *Micrasterias denticulata* and *Desmidium Swartzii* were abundant and thrived till September. The other forms either disappeared completely or were 'rare' or 'isolated' till the end of the season. *Cosmarium polygonum* was the only species of *Cosmarium* to be seen from the beginning of the season till the beginning of September. It was fairly common after the first showers, increased in number till the beginning of August, and then declined.

Of the Mesotaeniaceae, *Penium cucurbitinum* and *Cylindrocystis crassa* appeared in August and lasted till the end of the season, but neither of these forms was seen in remarkable number.

MYXOPHYCEAE: Only two members of the Myxophyceae, *viz.*, *Coelosphaerium Nagelianum* and *Lyngbya cryptovaginata* occurred at the beginning of the season, but within a month they completely disappeared. Towards the end of August *Lyngbya cryptovaginata* occurred again, became abundant towards the end of September and its numbers fell slightly in October.

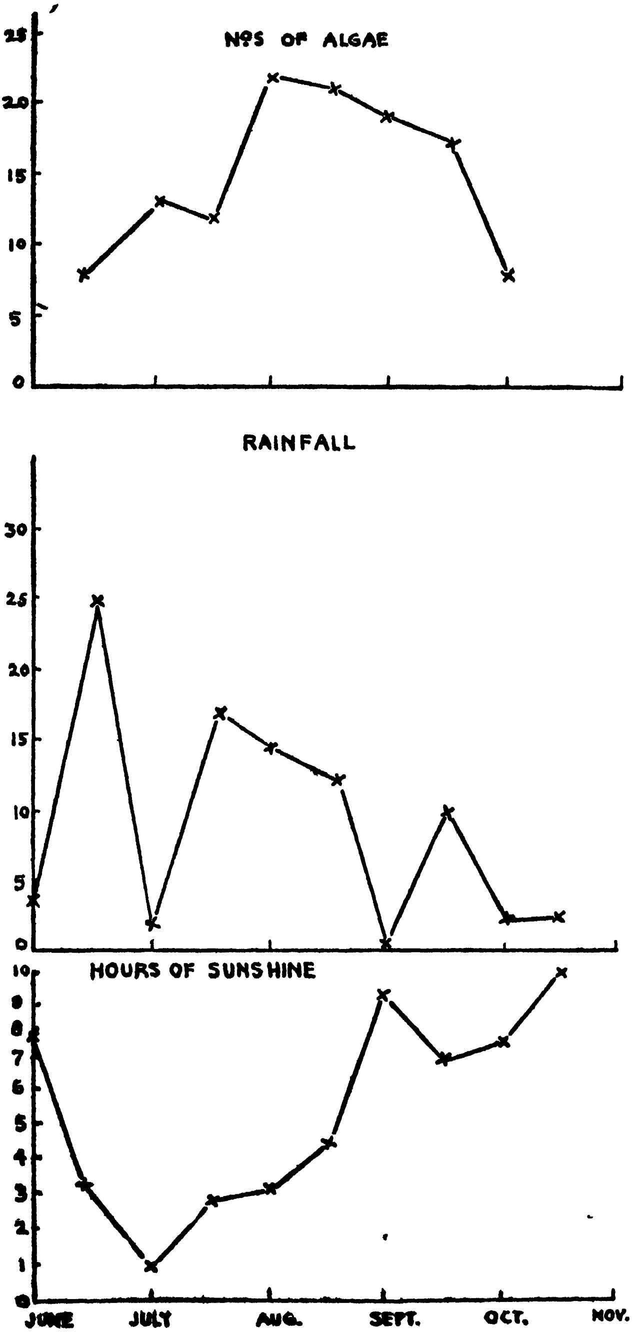

Fig. 1.

Graphs showing the relative numbers of algae and the meteorological data for the rainy season of 1940.

The relative number of species during the monsoon showed a definite correlation with sunshine, temperature and rainfall (*cf.* Fig. 1). At the beginning of the monsoon, only a few algae were seen. The maximum was reached in the beginning of August, after which the algae decreased, till in October there were only a few forms. *Oedogonium* and *Spirogyra* showed a mutual relationship, but *Spirogyra* was more prominent.

In these pools a large number of desmids was present. Taken as a whole, the unicellular forms reached their maximum much earlier than the filamentous species. Most of them were seen in abundance from the end of July to the middle of August, while the filamentous forms (except *Spirogyra Kuusamoensis*) reached their maximum between the end of August and the end of September. The desmids at the beginning of the season developed rapidly, but as the filamentous forms advanced in development, they seemed to interfere with the growth of these unicellular forms whose numbers diminished gradually.

COMPARISON WITH OTHER POOLS

The algal flora of the Jogeshwari pools is typical of the flora of road-side pools (Fritsch 1907, Iyengar 1940). It is characterised by the *Spirogyra-Oedogonium* association with *Spirogyra* as the more important type. Moreover a number of desmids, but very few members of the Chlorococcales are observed. The paucity of members of the Cyanophyceae further emphasises the resemblance to road-side pools. As these pools are very shallow, they dry up very quickly. Thus one day a pool may be full of water and a few days later completely dry. The change takes place very suddenly and new forms do not get a chance to develop. When, however, the pools are deeper, the change to the completely dry condition takes place more slowly and thus the changes in the concentration of the water allow for a corresponding change in the algal flora to take place, and hence we find the blue-greens replacing the greens in the Borivli pools (*cf.* Part I) and in some of the pools studied by Iyengar (1938) and Singh (1940). In the Jogeshwari pools, the two blue-greens that occur, were seen at the beginning of the season when the pools were first filled with water. After the first showers of rain, the concentration of the water must be fairly high, as a large amount of salts is washed down by the rains and dissolved in the water. Later as the rainfall becomes heavier, the water becomes very dilute and hence inhibitory to the good growth of blue-greens. A certain amount of algal succession is seen in these pools, but it is not so marked. The flora here scarcely bears any resemblance to the rock pools of Ceylon. As mentioned by Fritsch (1907) the rock pools are either very deep, or if shallow they owe their origin to springs. Thus the aeration is better and the temperature and light factors are also favourable to the good growth of algae. The pools studied here are shallow and stagnant, and only dependent on the rain and thus their flora is different. The depth of the pool therefore and the aeration obtainable, probably influence the composition of the flora and not the substratum alone.

The rain-water pools of Bombay are not strictly comparable with the rain-water pools in Northern India (Singh 1940) and Madras (Iyengar 1938, 1940), as the weather conditions in all these places are quite different. In Bombay, the monsoon lasts for 4½ months; so these pools remain full of water during this period after which they dry up, and remain so for the rest of the year unless under exceptional conditions Bombay has a spell of rain in January or February. In Northern India and Madras, there is never such continuous rain, with the result that the pools get filled up after a shower and are dry soon after. If there are intermittent showers of rain, they fill up and dry up repeatedly. Hence the same algae crop up again and again in such pools, though the blue-greens have been seen to replace the greens before the final drying of the pools. The pools studied here are very shallow and as they are dry very quickly, a large number of blue-greens do not get a chance to develop, as the conditions requisite for their development are over quickly.

In the monsoon the algae develop better in smaller pieces of water. The probable reason for this is, that the conditions necessary for growth and development and the proper concentration of the water are attained very soon in small pools, whereas in large ponds these conditions are established more slowly.

The filamentous species in these pools were reproduced sexually. The other forms probably survived in the same manner as the Borivli forms (*cf.* Part I). Thus it is possible that the vegetative and reproductive parts of algae distributed by wind and overflow waters reach these small pools from adjoining water areas and under favourable conditions germinate and make their appearance one after another. It is therefore necessary to study the distribution of the different species of algae in the other large and small bodies of water around these pools, as it may play an important part in the composition of the algal flora of these temporary static waters where ephemerals appear in rotation and finish their life histories in a brief space of time. Further investigations on these lines are in progress.

SUMMARY

1) The algal flora of a group of temporary, very shallow, rain-water puddles at Jogeshwari was noted during the monsoon of 1940.

2) The majority of the species were desmids. A few forms were seen at the beginning of the monsoon. They increased in number in the middle of the monsoon and decreased at the end.

3) Succession of the algae was not very obvious and the blue-greens were conspicuously absent. The reason for their absence is discussed.

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DESCRIPTION OF PLATES

Plate I

Fig. 1. *Scenedesmus bijugatus* (Turpin) Kütz. var *alternans* Reinsch x 406.
„ 2. „ *brasiliensis* Bohlin x 406.
„ 3. „ *obliquus* (Turpin) Kütz. x 406.
„ 4. *Cosmarium polygonum* (Näg.) Arch. x 406.
„ 5. „ *Quadrum* Lund. x 406.
„ 6. „ *binum* Nordst. x 182.
„ 7. „ *vexatum* West x 406.
„ 8. „ *asphaerosporum* Nordst. x 406.
„ 9. *Penium cucurbitinum* Biss. x 406.
„ 10. *Desmidium Swartzii* Ag. x 406.
„ 11. *Staurastrum Zahlbruckneri* Lutkem. forma Krieger x 188.
„ 12. *Cylindrocystis crassa* De Bary x 406.
„ 13. *Micrasterias denticulata* Bréb. x 35.

Plate II

Fig. 1. *Closterium acerosum* (Sch) Ehr. x 35.
„ 2. „ *moniliferum* (Bory) Ehr. x 182.
„ 3. „ *Dianae* Ehr. forma x 182.
„ 4. *Oedogonium hirnii* Gutw. x 182.
„ 5. „ *ahlstrandii* Wittr. x 182.
„ 6. *Ulothrix tenerrima* Kütz. x 406.
„ 7. *Lyngbya cryptovaginata* x 406.
„ 8. *Spirogyra* sp. x 182.
„ 9. *S. Kuusamoensis* Hirn. x 35.

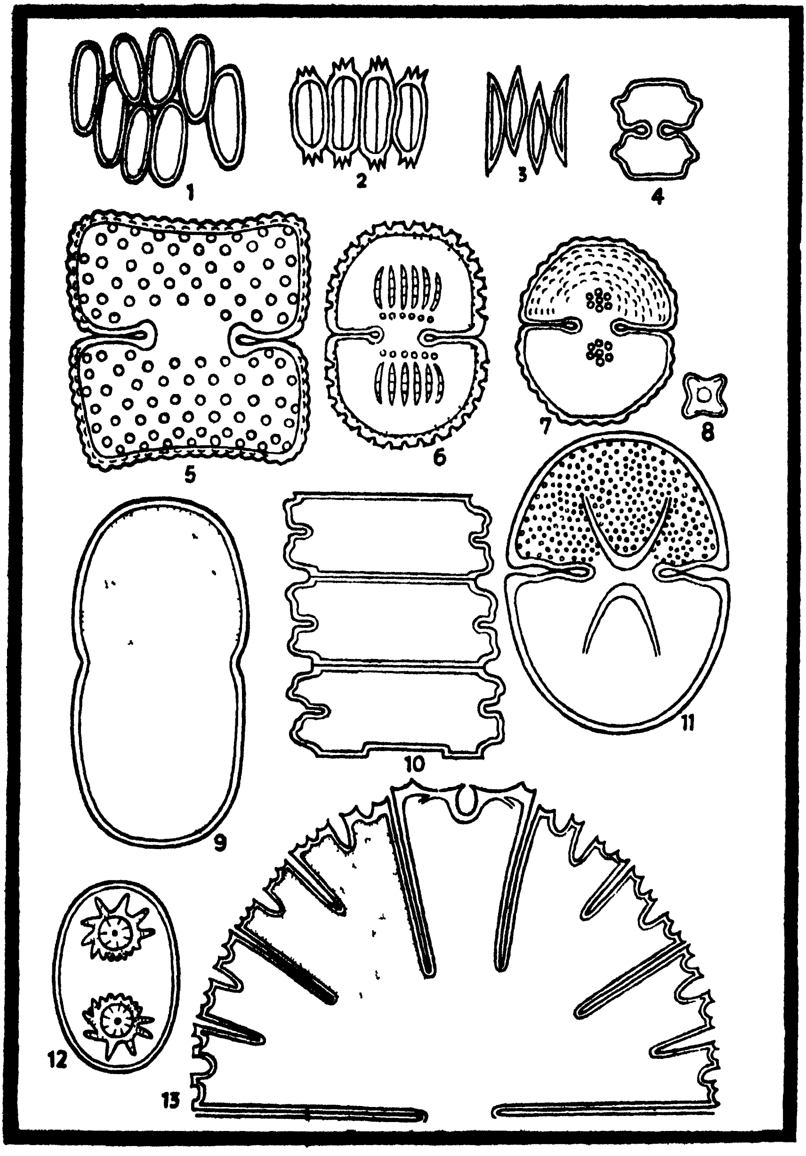

Plate I

The Algal Flora of Temporary Waters around Bombay:
Some of the algae in the rain-water puddles at Jogeshwari

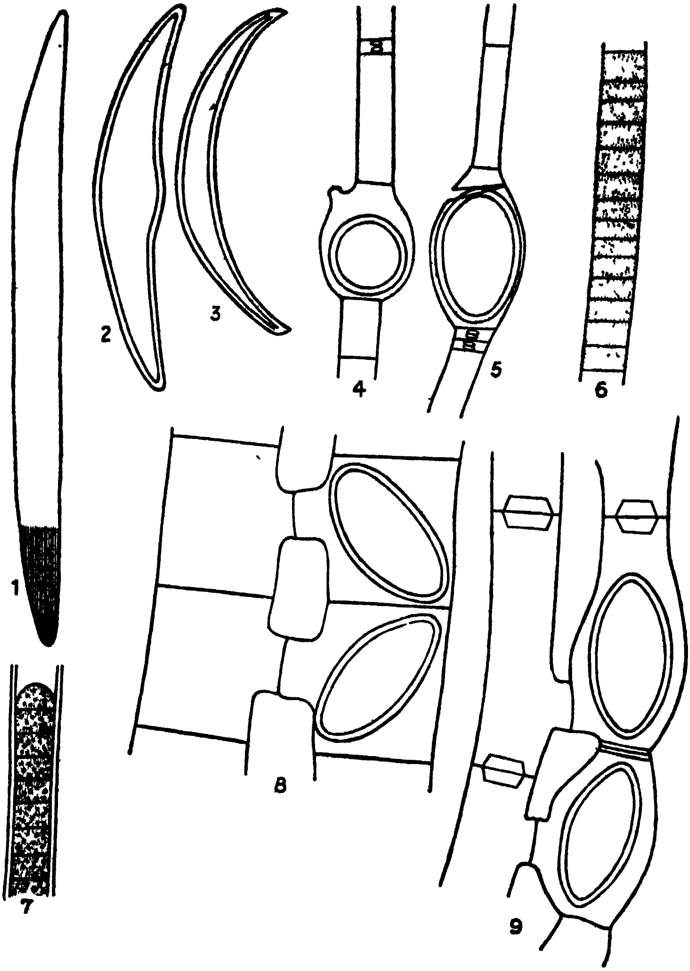

Plate II

The Algal Flora of Temporary Waters around Bombay:
Some of the algae in the rain-water puddles at Jogeshwari.

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